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OF THE USSR

(ZHURNAL PRIKLADNOI KHIMII)

IN ENGLISH TRANSLATION



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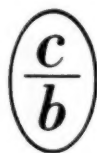
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# STATUS OF THE PRODUCTION OF PHOSPHATE FERTILIZERS BY ACID TREATMENT OF PHOSPHATES, AND IMMEDIATE PROSPECTS

D. L. Tsyrlin

The world production of mineral fertilizers developed at a rapid rate after the end of the Second World War (Table 1). The prewar level of mineral-fertilizer production, which fell considerably owing to the war, was regained in 1947. During the following 9 years it rose steadily and in 1956 it was 2.28 times the 1938 level, and exceeded 20,000,000 tons calculated as N,  $P_2O_5$ , and  $K_2O$ .

TABLE 1

Annual World Production of Mineral Fertilizers

Year	Production (1000's of tons) calculated as			Total
	N	$P_2O_5$	$K_2O$	
1938	2600	3500	2800	8900
1946	1850	2750	2000	6600
1947	2382	3916	2377	8675
1948	2918	4656	2804	10378
1956	6760	7187	6283	20230

The production of mineral fertilizers increased at an even greater rate in the USA, where the production level in 1956 was 5.6 times that of 1938 (Table 2).

The principal phosphate fertilizer at the present time is ordinary superphosphate, which comprises about 70% of the total world production of phosphate fertilizers. This is due to the simplicity of ordinary superphosphate production, the low production costs, relatively low capital outlay in plant construction, and the good agricultural qualities of the product.

Only small amounts (10-15%) of ordinary superphosphate are used as fertilizer in that form in the USA. Most of the superphosphate is used in the production of mixed fertilizers, of which about 90% is marketed as a triple mixture, containing all three essential nutrients (N,  $P_2O_5$ ,  $K_2O$ ) in various proportions. The range of mixed fertilizers available in the USA is very wide and varied. Superphosphate used for the production of mixed fertilizers is generally ammoniated, the ammoniation and mixing being effected in the same apparatus.

Ammoniation of superphosphate considerably improves the physical properties of mixed fertilizers. It is regarded as economically advantageous, as nitrogen in the form of ammoniated superphosphate is cheaper than in the form of nitrogenous fertilizers.

The production of triple superphosphate has greatly increased in the USA during the postwar years (Table 3); the output increased 5.3-fold during the past 10 years, reaching almost 1,400,000 tons in 1956.

TABLE 2

Production of Mineral Fertilizers in the USA

Year	Production (1000's of tons) calculated as			Total
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	
1938	240	620	287	1147
1956	2212	2252	2000	6464

TABLE 3

Production of Triple Superphosphate in the USA

Year	Production (1000's of tons)calculated as P <sub>2</sub> O <sub>5</sub>		Proportion of triple super- phosphate(%)
	ordinary	triple	
1946	1289	132	9.3
1956	1431	693	32.6

Most of the triple superphosphate in the USA is made with the use of wet-process phosphoric acid, made by the decomposition of phosphate rocks by means of sulfuric acid. The amount of triple superphosphate made with thermal-process phosphoric acid is relatively small, about 10-12%.

It seems likely that the high rate of increase of triple-superphosphate production is to some extent due to the fact that in the extraction of phosphoric acid from phosphate rocks a by-product is uranium, the content of which reaches 100-300 g/ton in some American phosphate rocks.

Among other forms of concentrated phosphorus fertilizers, mention must be made of ammonium phosphates, the production of which in 1956 was about 250,000 tons calculated as P<sub>2</sub>O<sub>5</sub>. According to published reports, several ammonium phosphate plants are now being built in the USA, and the production of this type of fertilizer is likely to increase considerably in the near future.

Calcium phosphate dihydrate, made by the sulfuric acid process, is used very little as fertilizer, as the relatively high consumption of sulfuric acid per unit of useful material in the product makes it less economical than other phosphate fertilizers made by the sulfuric acid process.

Calcium phosphate dihydrate is also produced as a fertilizer by means of hydrochloric acid decomposition of phosphates, with the use of cheap hydrochloric acid, obtained as a by-product in some other process. Plants for this purpose exist in Belgium and France, where hydrochloric acid is obtained as a by-product in potassium sulfate production.

The growth of concentrated phosphate-fertilizer production based on the sulfuric acid extraction of phosphates was accompanied by improvements in the plant equipment. The foreign fertilizer industry now has highly productive vacuum filters of new types (rotary, conveyer belt, band) for the separation of phosphoric acid from calcium sulfate; multichamber extractors, immersion pumps for slurries and phosphoric acid, high-quality acid-resistant filter fabrics, etc.

In recent years the production of mixed fertilizers based on nitric acid decomposition of phosphates has been developed considerably in a number of countries. The great interest in this process is due to its considerable technological and economic advantages over the sulfuric acid conversion of phosphates, and also to the sulfuric acid shortage in some countries.

The reason for the economic advantage of the nitric acid method is that in the decomposition of phosphate by nitric acid the chemical energy of the latter is utilized twice — for decomposition of the phosphate, and for the production of a nitrogenous fertilizer. In the decomposition of phosphate by sulfuric acid, the chemical energy of the latter is used once only, while the sulfuric acid is combined with the calcium from the phosphate to form calcium sulfate, which is an inert filler.

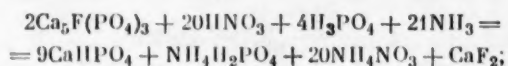
The methods now in use abroad for the nitric acid decomposition of phosphate may be divided into three main groups.

1) The production of a mixed fertilizer by the decomposition of phosphate by means of mixtures of nitric and phosphoric, or nitric and sulfuric acids, followed by ammoniation, drying, and granulation of the product.

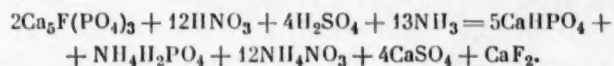


The reactions in this process can be represented by the following over-all equations:

in phosphate decomposition by nitric and phosphoric acids



in phosphate decomposition by nitric and sulfuric acids



For the production of a triple fertilizer, potassium chloride is added to the pulp after ammoniation. Sulfates (of ammonium, potassium, sodium, etc.) are sometimes used instead of sulfuric acid.

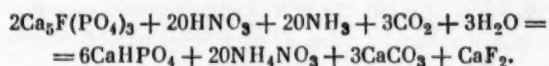
## 2) Decomposition of phosphate by nitric acid alone.

In this process, the amount of CaO in excess of the amount required for dicalcium phosphate is removed from the nitric acid extract by the freezing out of calcium nitrate  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , or in the form of the double salt  $\text{NH}_4\text{NO}_3 \cdot 5\text{Ca}(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$ , formed by addition of the appropriate amount of ammonium nitrate to the extract. The filtrate, after separation of calcium nitrate, is ammoniated.

3) The third group includes recent modifications in which carbon dioxide is used instead of sulfuric or phosphoric acid.

The process is carried out as follows. The phosphate is decomposed by nitric acid, and the resultant slurry is neutralized with ammonia. Before this, in order to prevent retrogradation of the  $\text{P}_2\text{O}_5$ , magnesium salts (mainly magnesium sulfate) are added to the slurry, in amounts equivalent to 2% of the final production. The slurry obtained after the neutralization is treated directly (without separation) with ammonia and carbon dioxide, to convert calcium nitrate into ammonium nitrate and calcium carbonate.

The reactions in this process may be represented by the following over-all equation



These processes are used for the production of mixed fertilizers with different N :  $\text{P}_2\text{O}_5$  :  $\text{K}_2\text{O}$  ratios, with up to 45% of total useful material.

The total USSR production in 1956 was 2,590,000 tons (calculated as N,  $\text{P}_2\text{O}_5$ , and  $\text{K}_2\text{O}$ ) of mineral fertilizers, including a considerable proportion of phosphates.

Of the total production of phosphate fertilizers, ordinary superphosphate comprised over 50%, and ground phosphorites (phosphate rocks), about 20%. Thus, the major part of the phosphate fertilizer output was in the form of ordinary superphosphate.

Concentrated phosphate fertilizers and mixtures are not being produced in the USSR. Relatively small amounts of mixed fertilizers are produced by the nitric acid decomposition of apatite concentrates, and some ammoniated superphosphate is made from Kara-Tau phosphorites. The prewar production of calcium phosphate dihydrate by the sulfuric acid method has been discontinued because it is unprofitable. The earlier production of mixed fertilizers has also been discontinued, as there is now no agricultural demand for them.

Ordinary superphosphate is made in our country from two types of phosphate raw materials – apatite flotation concentrate, and Kara-Tau phosphorites. In 1956, the former comprised about 86%, and the latter, about 14% (calculated on 100%  $\text{P}_2\text{O}_5$ ). The two products differ considerably both in contents of available phosphorus and in physical properties. Superphosphate from apatite concentrate contains up to 20% of assimilable  $\text{P}_2\text{O}_5$ , and has good physical properties (dry and free-flowing). Superphosphate from Kara-Tau phosphorites contains about 14% of assimilable  $\text{P}_2\text{O}_5$ , and has unsatisfactory physical properties (a smeary consistency). Superphosphate from Kara-Tau phosphorites becomes very moist when stored under humid conditions, and its physical properties deteriorate sharply.

Therefore in the production of superphosphate from Kara-Tau phosphorites it is necessary to take measures for improving its physical properties; this can be successfully achieved either by granulation or by ammoniation.

The unsatisfactory physical properties of superphosphate from Kara-Tau phosphorites are due to the presence of considerable amounts of dolomite in the latter (the MgO content is 4% and over); this gives rise to the very hygroscopic monomagnesium phosphate when the phosphorite is decomposed by sulfuric acid. The presence of monomagnesium phosphate in the superphosphate also has an adverse effect on the degree of decomposition of the phosphorite, as the high solubility of monomagnesium phosphate in phosphoric acid decreases the reactivity of the latter. The conversion coefficient of the phosphate in superphosphate from Kara-Tau phosphorites does not in practice exceed 88-89%, whereas in superphosphate from apatite concentrate it often 95-96%.

In view of the quality of the Kara-Tau phosphorites, and the great heterogeneity of the deposits, the problem of phosphorite beneficiation is of great importance. Work on the flotation-beneficiation of Kara-Tau phosphorites has involved considerable difficulties, and the process is still in the research stage.

Worthy of attention is the work of M. L. Chepelevetskii and E. E. Brutskus of the Scientific Research Institute of Fertilizers and Insectofungicides (NIUIF) on the chemical extraction of magnesium from Kara-Tau phosphorites (chemical beneficiation), based on selective solution of the dolomite in weak acids, without dissolution of the phosphate.

If a concentrate of acceptable magnesium content cannot be obtained by flotation, it may be possible to augment flotation by chemical beneficiation. It would then be possible, without excessive complication of the flotation process, to utilize the leaner ores from the deposits, and to obtain high-quality concentrate with low magnesium contents from them.

Considerable advances have been made in superphosphate production in our country during the postwar years. The main achievement has been the adoption of the continuous process, which marked the raising of superphosphate production to a new and higher technical level.

Conversion to continuous production has radically improved labor conditions and industrial hygiene in the plants, with a simultaneous increase of productivity and improvement of the superphosphate quality. Conversion to the continuous process has made automation of superphosphate production possible, and this has already been partially effected.

Granulated superphosphate is now being produced; this has considerable advantages over the powder, especially for row application. The proportion of granulated superphosphate in the total superphosphate production in 1956 was 24.5%.

The continuous production of ammoniated superphosphate from Kara-Tau phosphorites has been effected on the pilot-plant scale.

In view of the considerable increase of fertilizer production planned in the USSR in the near future,\* the production of ordinary superphosphate will also increase considerably; it is likely that ordinary superphosphate will remain the main phosphate fertilizer used in our country for a considerable time.

Apart from the further intensification, mechanization, and automation of the existing production, this fact raises even more acutely such problems as the following in the superphosphate industry:

- 1) decrease of sulfuric acid consumption and increased utilization of the phosphate raw materials;
- 2) decrease of the superphosphate aging time without a lowering of the phosphate-conversion coefficient;

\* The Directives of the XXth Congress of the CPSU in relation to the Sixth Five-Year Plan for the development of the national economy provide for an increase in the output of mineral fertilizers to 19,600,000 tons in 1960; i.e., double the 1955 production.

- 3) development of a continuous process of superphosphate production, obviating the need for storing;
- 4) radical improvement of the quality of superphosphate from Kara-Tau phosphorites;
- 5) improvement of superphosphate granulation, including the development of a highly productive granulation process without drying;
- 6) ammoniation of superphosphate by means of ammoniates, and the production of mixed fertilizers on this basis.

Possible routes to the solution of some of these problems may be illustrated by the following examples.

E. E. Zusser (NIUIF) has suggested and studied a method of superphosphate production with partial decomposition of phosphate by hydrochloric acid.

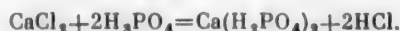
The method is as follows. About 75 weight parts of phosphate is decomposed by sulfuric acid in a quantity equivalent to 100 weight parts of phosphate, and superphosphate is made by the usual den process. Because of the high sulfuric acid ratio, a high degree of phosphate decomposition is reached even in the den stage.

The remaining 25 weight parts of phosphate is decomposed by 15-18% HCl, to yield a slurry containing dissolved phosphoric acid and calcium chloride



The superphosphate and slurry are then mixed, with addition of recycled product, and dried. The free phosphoric acid present in the den superphosphate and the slurry then interacts with calcium chloride to form monocalcium phosphate and hydrogen chloride; the latter is volatilized during the drying and absorbed to give hydrochloric acid, which is returned to the process.

The reaction during the superphosphate drying can be represented as:



Superphosphate obtained from Kara-Tau phosphorites by this process contains about 17% available  $\text{P}_2\text{O}_5$ , 2-3% free  $\text{P}_2\text{O}_5$ , and 0.3-0.4% HCl. The degree of conversion of the phosphate in the product is about 92%. The product is obtained in granulated form, and has good physical properties.

Thus, the superphosphate process with partial decomposition of phosphate by hydrochloric acid provides simultaneous solutions to several problems: a continuous process can be effected without intermediate aging of the superphosphate, the superphosphate quality can be improved considerably, the conversion of the raw phosphate can be raised (in the case of Kara-Tau phosphorites), and the sulfuric acid consumption can be diminished.

The author of this paper, in a study of the effects of the grinding fineness of apatite concentrate on the kinetics of its decomposition in superphosphate, found that fine grinding of apatite concentrate by vibratory milling leads to a considerable increase of the conversion coefficient of apatite, both in fresh superphosphate, and during subsequent storage. Thus, with 70 parts of sulfuric acid per 100 weight parts of apatite concentrate, the conversion coefficient of the apatite in the superphosphate reaches 95-97% on the fifth day, as compared with 90% obtained with apatite concentrate ground in the usual manner.

Thus, the aging time of the superphosphate can be decreased considerably, the conversion coefficient of the raw phosphate can be raised, and the sulfuric acid consumption lowered, by vibratory grinding of apatite concentrate. Moreover, with vibratory grinding of the apatite concentrate, the productivity of the apatite flotation plant can be increased without extension of the plant. Fine grinding of apatite concentrate is most suitable as a means of additional comminution of the concentrate obtained by flotation. It is then possible to modify the degree of grinding of the apatite ore before flotation to the optimum particle size for flotation, which corresponds to about 25% residue on a 0.15 mm screen.\* The productivity of the flotation unit (including the grinding, flotation, filtration, etc. equipment) is thereby raised by about 15%.

\* By the existing GOST for apatite concentrate, the residue on a 0.15 mm screen must not exceed 14%.

A. I. Shereshevskii (NIUIF), in a study of the degree of grinding of Kara-Tau phosphorites and the kinetics of their decomposition in superphosphate, also found that vibratory grinding of phosphorite is effective. However, the effect of fine grinding was less for Kara-Tau phosphorite than for apatite concentrate, and prolonged aging of the superphosphate was still necessary. This effect was probably associated with the harmful influence of magnesium, which is not avoided as the result of fine grinding of Kara-Tau phosphorites.

As already stated, concentrated phosphate fertilizers are not being produced in our country at present, but, in accordance with the Directives of the XXth Congress of the CPSU on the Sixth Five-Year Plan, their production is to be organized on a large scale in the near future. Thus, the production of concentrated phosphate fertilizers must reach 1,000,000 tons per year by 1960.

The scientific and technical basis for this achievement has already been adequately prepared. The production technology of triple superphosphate, ammonium phosphate, diammonium phosphate, and calcium phosphate dihydrate from domestic raw materials — apatite concentrate and various phosphorites — has been studied and mastered on the large pilot-plant scale, based on the sulfuric acid extraction of phosphates.

As the result of these studies, the planning of factories for the production of triple superphosphate from apatite concentrate and of ammonium phosphate from phosphorites is being completed. The production of modern Russian equipment for the production of phosphoric acid by the wet process is a matter of great importance in relation to these projects.

We are faced with the following main tasks in the production of concentrated phosphate fertilizers.

1. The production of modern equipment for wet-process phosphoric acid, and in particular of rotary vacuum filters, and centrifugal immersion pumps for phosphoric acid and slurry.

2. Further improvement of the technological processes for the production of concentrated phosphate fertilizers.

- a) Increase of the concentration of wet-process phosphoric acid, in order to shorten or eliminate the evaporation stage. As the result of work on the stability of different forms of calcium sulfate in phosphoric acid solutions in relation to their concentration and temperature, and to the presence of impurities, increase of the concentration of wet-process phosphoric acid in the "dihydrate" process from 25-27% to about 35%  $P_2O_5$  must be regarded as feasible. In the "anhydrite" process, the concentration of wet-process phosphoric acid may reach 45-50%  $P_2O_5$ .

- b) Improvement and intensification of the evaporation of phosphoric acid. The evaporation of phosphoric acid in bubbler equipment is now used. It is likely that the use of equipment of the Venturi-tube type for this purpose could result in considerable intensification of phosphoric acid evaporation.

- c) Development of continuous processes of triple superphosphate production (such as the process with the partial use of hydrochloric and sulfuric acid, fine grinding of the phosphate for the second process stage, etc.).

3. Study and development of technological processes for the production of new types of highly concentrated fertilizers, such as potassium and ammonium metaphosphates.

In the field of nitric acid conversion of phosphates the following processes have been studied and carried out on the pilot scale here: production of calcium phosphate dihydrate and calcium nitrate, and production of N-P-K fertilizer. Both processes have been studied in relation to apatite concentrate.

In the first process, ground limestone is added to the slurry formed by the nitric acid decomposition of apatite; the precipitated dicalcium phosphate dihydrate is filtered off and dried, and the calcium nitrate solution is evaporated to yield the crystalline product.

In the second process, part of the calcium nitrate is crystallized out at reduced temperature. The residual solution is neutralized with ammonia, potassium chloride is added, and the slurry is dried. The more calcium nitrate is frozen out of the solution, the more water-soluble  $P_2O_5$  is present in the N-P-K fertilizer.

The following tasks confront us in the field of nitric acid conversion of phosphates:



1) Improvement of the studied processes for the production of calcium phosphate dihydrate and N-P-K fertilizer, with regard to continuous precipitation, and crystallization of calcium nitrate;

2) development of new processes for the production of mixed fertilizers by the decomposition of phosphate with mixtures of nitric and sulfuric acid, and with the use of carbon dioxide instead of sulfuric acid.

The following conclusions may be drawn from the review [1-7] of the state of phosphate fertilizer production in our country by the acid conversion of phosphates.

1. Our principal phosphate fertilizer is ordinary superphosphate, produced in powdered and granular form. The production of superphosphate will continue to increase, and this type of fertilizer will be of predominant importance for the next 5-10 years.

2. In addition to the increase of ordinary-superphosphate production, the production of concentrated-phosphate fertilizers will be organized in the next few years, and the relative proportion of these in the total phosphate fertilizer production will undoubtedly increase year by year.

The production of concentrated fertilizers is a very urgent problem in our country, in view of the extensive territory and the great distance over which fertilizers must be transported.

The importance of this fact may be illustrated by the following data (based on the calculations of Ia. A. Ioffe, NIUIF): the rail-transport costs for superphosphate in 1955 totalled about 160,000,000 rubles, and the costs of transport from the railroad to the fields and the application to the land were approximately 340,000,000 rubles more. If the same amount of  $P_2O_5$  had been produced as triple superphosphate, the savings in transport and application would have been about 300,000,000 rubles per year at the 1955 production level.

A second and no less important fact is the presence of considerable reserves of phosphorites in our country; these are not of suitable quality for superphosphate production, but can be successfully used as a source of concentrated fertilizers.

3. The production of mixed fertilizers by nitric acid conversion of phosphates is to be organized on a fairly large scale in the next few years.

4. A task due for consideration is the organization of mixed granulated fertilizer production by the ammoniation of ordinary and triple superphosphate by means of ammoniates.

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# TREATMENT OF TECHNICAL ALUMINA AND STUDY OF SOME OF ITS PROPERTIES FOR CHROMATOGRAPHIC SEPARATION OF INORGANIC CATIONS

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Several methods are known for the preparation of aluminum oxide for chromatography; they are based on prolonged heating of technical alumina in the 300-1000° range [1-3]. The simplest and most rapid method was that proposed by Gapon [1]. This method yields an active product in 5-10 minutes at 800-900°. However, the preparation of high-quality products involves a number of difficulties and unexplained effects [4], such as limited activity, solubility in chemical reagents, heterogeneity of the adsorbent, etc.

We studied the activation of technical alumina in relation to the heating conditions and the alkali content.

There are several methods for determination of the quality of active alumina [5], and several methods of rating [6]. Some of these are quite unsuitable for alumina used in chromatography of inorganic salts in aqueous solutions, while others give rise to considerable errors. For example, rating of the product by its water content, as recommended by Kaplan and Meller [6], is quite unsuitable for this purpose, because differences of water content of similar products have no significant influence on the formation of chromatograms by aqueous solutions of inorganic salts.

Considerable inaccuracies sometimes arise in determination of alumina activity by means of methylene blue, very commonly used for evaluation of sorbent quality [5]. The sorption of this dye depends on the temperature and concentration; it can be salted out [7] and may undergo desorption in the course of time.

The simple method proposed in 1953 by Fricke [8] for evaluation of alumina quality by sorption of  $\text{CuCl}_2$  also involves errors. It does not take into account the possible formation of multimolecular layers on the sorbent [9], or the formation of basis salts [10] other than  $\text{Cu}_2(\text{OH})_2\text{Cl}$  on which the calculation is based.

The activity of alumina intended for chromatographic separation of inorganic cations depends mainly on its alkalinity and crystal structure [1,8,11]. Three types of contaminating alkali have been established in alumina - insoluble, leachable, and unleachable - and it has been found that occluded alkali forms sodium aluminate with the crystalline substance on heating [12].

Heating results in a number of complex effects within the crystals and on their surfaces: the crystal lattice is dislocated, water is liberated, access within the crystals becomes easier, and a series of phase transitions is effected, through hydrargillite - bayerite, boehmite - diaspor - alumina [13]. Boehmite was found to be the most active crystal form [8].

When a suspension of alkaline alumina reacts with 0.001-1 N acids, two stages are clearly distinguished. The reaction rate is high at the first, and low at the second.

The chromatographic effectiveness of calcined alumina increases with increasing content of rapidly-titratable alkali. A high content of carbonate alkali makes this adsorbent unsuitable for chromatography in acid solution, because of the liberation of  $\text{CO}_2$  which destroys the chromatograms.

An extensive surface and visible porosity in crystalline alumina aggregates favor the retention of precipitates on them. Therefore alkaline alumina can be regarded both as a support and a reagent.

For evaluation of the quality of alkaline alumina samples, their quantitative content of rapidly-titratable alkali is important, although unfortunately it is not strictly controlled in commercial preparations.

For improvement of the quality of alumina used for chromatographic separation of inorganic cations, we treated alumina with caustic soda, sodium silicate, and sodium phosphate by wet and dry processes. According to Kurnakov [14], the reaction of sodium silicate with alumina may result in the formation of a zeolite of the composition  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot n\text{H}_2\text{O}$ .

## EXPERIMENTAL

The raw material for the production of active alumina was powdered aluminum hydroxide of Russian origin. The weight loss on calcination was 32.4% at 500°, and 32.56% at 900°. In the calcined state it corresponded to grades G<sub>0</sub>-G<sub>3</sub> according to TsMTU\* 953-41, and contained (in %):  $\text{Al}_2\text{O}_3$  97.6-98.29,  $\text{SiO}_2$  0.25-0.04,  $\text{Fe}_2\text{O}_3$  0.05 - 0.03,  $\text{Na}_2\text{O}$  0.6, calcination loss 1.50-1.

When the uncalcined hydrated alumina was heated in a porcelain basin or crucible, the powder moved in a manner resembling the boiling of a liquid (Table 1).

TABLE 1  
Effect of Heat on Powdered Aluminum Hydroxide

Time (minute)	Temperature (deg)	State of powder
0	50	} Still
5	200	
7	280	} Intensive "boiling"
10	300	
13	360	
15	400	
25	800-900	Gentle "boiling"

Aqueous extracts obtained when calcined and uncalcined alumina was shaken with hot water for 5 minutes gave a color with phenolphthalein. The uncalcined product did not give a color in cold water.

Optical microcrystallographic examination of different alumina samples showed that the active and inactive particles can always be distinguished by means of the qualitative reaction with methylene blue; the former are colored, and the latter are not. The uncalcined material, and the alumina calcined at temperatures above 1000°, were inactive. In the other cases the particles were stained to different extent.

For quantitative determination of the activity of different alumina preparations by means of methylene blue, we used the excess method [5], and found

that sorption of this dye is especially rapid during the first few minutes, then it diminishes, and after several hours the dye is almost completely desorbed. It is therefore impossible to use methods in which solutions of methylene blue are left to act on 1-2 g of the dry sorbent for a long time (several days).

Stirring of the suspension had little effect on sorption of the dye. Therefore in the hydrodynamic sense the sorption of methylene blue on alumina is a process of internal diffusion. Consequently, as soon as the alumina particles become suspended in the dye solution as the result of stirring, further intensification of the stirring is superfluous.

The sorption of methylene blue decreases with increase of suspension temperature, and increases with the dye concentration. However, the Freundlich equation  $\alpha = \beta C^\mu$  does not represent satisfactorily the adsorption of methylene blue on activated alumina, because of the observed desorption and salting out of the dye by water-soluble impurities in the alumina.

The most consistent results in determinations of alumina activity with the aid of methylene blue were obtained by brief interaction of the components at constant temperature by the following technique: 50 ml of solution containing 1000  $\gamma$  of methylene blue was placed in a cylinder with a ground-glass stopper, 0.1 g of alumina powder was added, and the suspension was mixed for 5 minutes by inversion of the cylinder. The solid particles were then separated from the liquid by centrifugation or filtration through a glass filter, and the liquid was analyzed colorimetrically, either by the visual method or by means of the photocolormeter [15].

\*Specifications for Nonferrous Metallurgy.

This method gives results similar to those obtained in determinations of alumina surface by means of  $\text{CuCl}_2$  [8].

This method could be used for observation of changes in the sorptive properties of alumina under various experimental conditions.

Variations of the activity of alumina with the calcination time are given in Table 2. It is seen that rapid calcination (5-10 minutes) is better than slow calcination for development of sorptive properties in the product; this is in good agreement with Gapon's findings [1].

Data on the influence of particle size on alumina activity are presented in Table 3. It follows from Table 3 that variations of the dispersity of the chromatographic alumina have little effect on its technical properties.

The surface of 1 g of technical alumina, calcined for 5 minutes at  $900^\circ$ , was determined by means of  $\text{CuCl}_2$  [8], and methylene blue, calculated from the value of the area occupied by a molecule of this dye [16]. The surface area was found to be in the  $30\text{--}33\text{ m}^2$  range.

Alkali is washed out much more rapidly by water from calcined than from uncalcined alumina. The capacity of the chromatographic aluminas for methylene blue decreases as a result. It is possible to wash out alkali from calcined alumina either to a definite limit, or to a neutral reaction. The apparatus used for steam distillation of organic substances was used for the washing; in this way local overheating of the suspension was avoided, vigorous agitation was achieved, and the washing was accelerated appreciably. Such treatment of calcined alumina yields different preparations of fixed capacity for methylene blue, which remains unchanged after they have been dried at  $110^\circ$ , or calcined again for 5 minutes at  $900^\circ$ .

TABLE 2

Effect of Calcination Time of Aluminum Hydroxide on the Activity of  $\text{Al}_2\text{O}_3$

Temperature (deg)	Time (minutes)	Sorption of methylene blue ( $\gamma$ )
900	0.5	510
	1	720
	2	645
	3	700
	4	640
	5	710
	15	620
750	30	325
	30	230

TABLE 3

Effect of  $\text{Al}_2\text{O}_3$  Dispersity on its Activity

Sieve holes per $1\text{ cm}^2$	Grain size ( $\mu$ )	Sorption of methylene blue ( $\gamma$ )
900-2500	68-184	720
2500-3600	68-120	725
3600-4900	76-104	665
4900-10000	48-72	710

The activity of calcined alumina toward methylene blue also decreases after treatment with acid solutions; this can be ascribed to total or partial neutralization of the alkali. For example, the sorption capacity of the alumina for methylene blue

fell to zero after the calcined powder had been shaken for 5 minutes with excess HCl of 0.1-0.01-0.001, normality and then washed with water to a neutral reaction to methyl orange.

Since acid solutions are generally used in the chromatographic separation of cations, we determined the solubility of alumina, calcined at  $900^\circ$ , in hydrochloric, sulfuric, and nitric acids. It was found that when 0.2 g of alumina was left in contact with 50 ml of 0.1-1 N HCl at  $20^\circ$  the solubility reached 0.95-1.1%. The solubility as the result of 5 minutes of stirring in 0.1 N nitric and hydrochloric acids was 0.3-0.5%, in 0.1 N sulfuric acid, 0.1%, in water at  $20^\circ$ , 0.015%, and in water at  $90^\circ$ , 0.033%.

The course of interaction of  $\text{Al}(\text{OH})_3$  and  $\text{Al}_2\text{O}_3$  with 0.1 N HCl was also studied by the changes of pH when 1 g of the substance was left to stand with 30 ml of the acid. For comparison, a similar sample was left in a closed vessel with water. The pH was determined potentiometrically and colorimetrically. The results are given in Table 4.

These values are in good agreement with the pH values of aqueous alumina and aluminum hydroxide suspensions found by Gromov [17] (3.26-4.43), Aksel'rud and Fialkov [18] (3.54-4.21), and Britton [19] (4.1). The data in Table 4 demonstrate the buffer action of alumina samples during brief or lengthy chromatographic separations of inorganic cations.

TABLE 4

Variations of pH of  $\text{Al}(\text{OH})_3$  and  $\text{Al}_2\text{O}_3$  Suspensions with Time

Substance	Amount of reagent (ml)	pH after standing time (hours)					
		1	24	48	120	240	2400
$\text{Al}(\text{OH})_3$	Water 80	9.96	—	8.4	—	—	8.1
	HCl 80	2.00	—	2.05	—	—	3.75
$\text{Al}_2\text{O}_3$	Water 80	—	8.8	8.1	8	—	8.1
	HCl 80	—	1.9-2.14	3.64-3.7	4-4.01	—	4-4.02
	HCl 15	—	4.5	—	—	4.4	—
	HCl 8.2	—	4.9	—	—	5.25	—

The treatment of alumina with sodium silicate in order to improve its activity for chromatography was performed as follows: 1-5 g of alumina was left in contact with sodium silicate solution for 24 hours, with stirring, and the powder was then separated off by centrifugation or by filtration through a coarse paper filter. It was then dried in air, and in some cases additionally calcined at 900°. The capacity of the sorbent for methylene blue before the treatment was 975  $\gamma$ . The changes in the activity of  $\text{Al}_2\text{O}_3$  after treatment with sodium silicate are given below.

(1) $\text{Na}_2\text{SiO}_3$ content of solution (%)	20	10	5	2.5	1.25	0.5	0.25
(2) Capacity of sorbent for methylene blue ( $\gamma$ )							
(3) after air treatment and drying	270	310	630	960	900	940-970	
(4) after calcination at 900°	375	540	760	835	960	980	960-970

These results show that the activity of alumina is not increased by treatment with sodium silicate. The activity decreases considerably with increase of the  $\text{Na}_2\text{SiO}_3$  concentration of the solution used.

The activity toward methylene blue of the zeolite synthesized by Kurnakov's method [14] was no lower than that of alumina. For example, 0.1 g of the air-dried zeolite adsorbed 980  $\gamma$  of methylene blue, and after calcination for 5 minutes over a gas burner, 970  $\gamma$ . This suggests that wet and dry treatments decrease alumina activity as the result of disturbance of the fine surface structure of the powder, with decreased permeability of the particles, rather than as the result of zeolite formation.

The following results were obtained when alumina was treated with NaOH solutions: the uncalcined technical aluminum hydroxide was left for 12 hours in 2 N NaOH, then washed lightly with water, dried in air, and used for chromatography of inorganic cations; the uncalcined material did not yield chromatograms, while the calcined product gave the same chromatograms as those obtained on ordinary calcined alumina.

Similar treatment of calcined alumina increased its activity, and the intensity of the chromatographic zones increased accordingly. However, frequent repetition of this impregnation and calcination procedure, for further increase of the activity, had an adverse effect on the quality of the alumina and led to distorted chromatograms.

Repeated alkaline treatment of alumina is to some extent similar to the fusion of minerals with caustic soda or sodium carbonate, used in analytical practice. There is no doubt that calcination results in the formation of a melt which blocks the sorbent micropores. A similar effect is observed if alumina is treated with the fusible sodium phosphate.



Consequently, although a single alkali impregnation and calcination makes the alumina more active, repetition of these combined treatments lowers the activity because of pore clogging.

The alkali is distributed more uniformly through the crystalline material when the latter is precipitated from mother liquors, than in the usual impregnation of alumina by means of alkaline solutions. This largely explains the valuable properties of crystalline alumina of factory origin as a raw material for the preparation of alkaline materials which form good chromatograms in the separation of inorganic cations.

#### SUMMARY

The effects of the calcination conditions and alkali content on the activation of technical alumina were studied; the influence of rapidly-titratable alkali on the characteristics of the samples and their buffer action was demonstrated.

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## THE PRODUCTION AND USE OF ALKALI ORGANOSILICON SILICATES

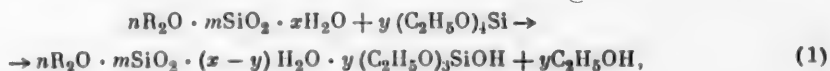
V. A. Matveev, G. D. Nessonova, and M. A. Matveev

Water glass is a mineral binder and adhesive which is widely used in many branches of industry. However, in a number of cases it does not conform to the requirements of modern technology. Water-glass films dry slowly, and swell strongly when heated to form a porous, mechanically weak mass. Solid alkaline sodium silicate is usually dissolved in autoclaves. A new product with very valuable properties was obtained by the reaction of alkali-silicate solutions with ethyl orthosilicate (tetraethoxysilane). This was a solid, elastic, white substance, easily powdered, and readily soluble in water; it was given the name of organosilicon silicate, OS (OS-Na from sodium silicate, and OS-K from potassium silicate) [1, 2].

The formation of compounds of this type was later confirmed by Henglein and Krohe [3], who obtained gels, which they named silicanol gels, by the reaction of silicic acid with methyl silanol in an alkaline medium.

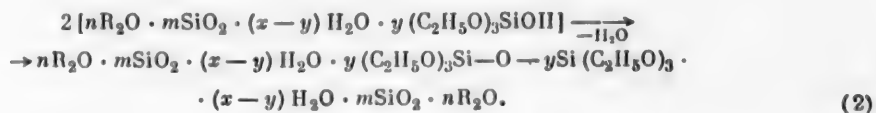
The chemical reactions of tetraethoxysilane with sodium silicate may be represented as follows:

hydrolysis of tetraethoxysilane with formation of triethoxysilanol hydrosilicate according to the equation



where  $R_2O$  is an alkali-metal oxide;

condensation of the hydrolysis products according to the equation



These equations show that complex organosilicon silicates of high molecular weight may be formed, containing new siloxane bonds and alkoxy groups.

These chemical processes result in considerable dehydration of the original water glass solution, and increase of the silica ratio.

All these facts lead to a number of valuable technical properties in the new product, the organosilicon silicate: decreased swelling on heating, improved wetting and adhesive powder, better heat resistance and dielectric properties.

The technological process for the production of organosilicon silicates is very simple. OS is formed by the mixing of two liquids — water glass and tetraethoxysilane. The optimum proportions of water glass and tetraethoxysilane were determined in a study of the process.

Table 1 contains data on the reaction products of water glass and tetraethoxysilane taken in various proportions; the external appearance and the degree of swelling on heating are given. For determination of the swelling, a film of 0.2 g of the substance was applied over an area of 4 cm<sup>2</sup> on a metal plate (Steel 45).

The films were dried in the drying oven at 60-70° for 30 minutes, and the plates were then heated in a muffle furnace at 500°. The films lost their transparency, became white, and formed porous masses. The degree of swelling was determined in terms of the height of the porous mass (average values of five measurements).

It is seen from the data that clear separation of two phases – solid and liquid – when water glass and tetraethoxysilane are mixed commences at 3 : 2 ratio of the reagents. The solid so formed is soluble in water; the solution forms a smooth transparent film, but when heated to 500° this film still swells considerably. The solid substance obtained at 1 : 1 ration of water glass to tetraethoxysilane is also readily soluble in water; the solution forms a smooth transparent film on the metal plate, but this film changes little in volume when heated at 500°. The swelling of films from the original water glass is 6-7 times as great as that of OS films.

TABLE 1

Characteristics of the Reaction Products of Water Glass and Tetraethoxysilane

tetraethoxy- silane	Amount of reagents (%)	Appearance of mixture after 2 hours of stirring	Nature of coating on metal plate	Swelling (mm)	Notes
	sodium sili- cate (sp. gr. 1.26, silica ratio 2.57)				
0	100	Transparent col- loidal solution	Smooth transparent colorless film	6-7	Easily applied onto metal plate
1	99	Slightly turbid solution	Smooth film	6-7	} Ditto
10	90	Turbid solution	Turbid film	6.0	
20	80	Ditto	Ditto	5-6	Film applied in a thick layer
50	70	Gel and oily liquid distinguishable	Film not formed	—	Not coated
40	60	Distinct separation of solid and liq- uid phases	Smooth transparent colorless film	8	Film formed from solid phase dis- solved in water
50	50	} Ditto	Ditto	1.1	} Ditto
60	40			1.1	
70	30			1.1	
80	20			1.1	

When the organosilicon silicate is dissolved in water, a colloidal solution is formed with good gluing properties, and high adhesion to various materials, especially metals.

If a solution of organosilicon silicate is treated with tetraethoxysilane, a solid phase is again formed; this was named secondary organosilicon silicate OS<sub>2</sub>; it is also readily soluble in water.

Experiments showed that the chemical composition of the organosilicon silicates formed by repeated treatment of tetraethoxysilane alters, with an increase of the silica content and a decrease of the alkali content; i.e., the silica ratio increases in the sequence OS<sub>1</sub>, OS<sub>2</sub>, etc. If crude water glass is used, the increase of the silica ratio is accompanied by chemical removal of impurities (iron compounds, etc.).

The results of chemical analyses of water glass (technical) and of the organosilicon silicates made from it are given in Table 2.

#### Properties of Alkali Organosilicon Silicates

Organosilicon silicates are readily soluble in water, alkalies, phenol, ethylene glycol, and glycerol, but are not soluble in ligroin, benzene, acetone, and ethyl alcohol. They do not dissolve in mineral acids, but lose their original properties – solubility in water adhesive power, etc.



TABLE 2

Chemical Composition of Water Glass and Organosilicon Silicates

Silicates	Chemical composition, calculated for the calcined substance (%)			Silica ratio $\frac{\text{SiO}_2}{\text{Na}_2\text{O}}$
	SiO <sub>2</sub>	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub> etc.	
Water glass	68.28	27.99	4.88	2.57
OS <sub>1</sub>	70.87	24.94	8.20	2.98
OS <sub>2</sub>	73.98	28.99	2.64	8.16
OS <sub>3</sub>	78.84	20.76	0.40	8.92

Data on the water solubility of OS-K, made from potassium silicate of sp. gr. 1.285 and 2.6 silica ratio, are presented below.

## Solubility of OS-K in Water

Amount of OS dissolved in 100 g of water (in g)	Solution concentration (%)	Specific gravity of solution
50	33.3	1.076
100	50.0	1.117
150	60.0	1.145
200	66.6	1.162
250	71.4	1.180
300	75.0	1.193
400	80.0	1.216

The binding power of OS was determined from the tensile strength of standard 8-shaped specimens made from Liubertsy sand sifted through a screen with 4 holes/cm<sup>2</sup>, with different contents of powdered OS-Na as binder.

TABLE 3

Results of Tensile Tests on Molded Specimens

Composition of specimen (wt.%)		Moisture content at molding (wt. %)	Tensile strength (kg/cm <sup>2</sup> )
OS	Sand		
3	97	5.1	14
5	96	5.0	23
7	93	5.2	30
10	90	4.8	35

The molded specimens were dried in the drying oven for 1 hour at 110°, and then tested for tensile strength. The results of these tests are given in Table 3.

The adhesive strength of OS was determined from the load necessary to detach strips of strong linen cloth attached to plates of Steel 45 over an area of 2 x 3 cm, and from the shearing force applied to two metal plates glued together over an area of 2 cm<sup>2</sup>. In the former case, the tests were performed on specimens dried in the drying oven at 70-80°. In the latter case, the specimens were dried in the oven at 110° and calcined in a muffle furnace at 600° for 1 hour.

The experiments were performed with OS solution made from sodium silicate of silica ratio 2.6; the specific gravity of the water glass and the OS-Na solution was 1.25.

The results of the tests are given in Table 4.

Table 4 shows that the OS joint between metal plates had a shear strength of 2 kg/cm<sup>2</sup> after being heated an hour at 600°, whereas plates joined by water glass under the same conditions could be easily separated by hand.

TABLE 4

Results of Tests on the Adhesive Power of OS

Adhesive	Load, kg		
	tensile at 20°	shear strength at 20°	after heating to 600°
Sodium silicate	1.7	29.0	0.0
OS	1.8	31.0	2.0

Comparison of the drying rates of films made from water glass and from OS of the same density made from it showed that OS films dry much more rapidly than water-glass films at the same temperature.

**Electrical insulation properties.** For comparison of the insulating properties of water glass and organosilicon silicates, the electrical conductivity of solutions of potassium silicates of 2 and 2.75 silica ratios, and of OS made from them, was compared. The specific gravity of all the solutions was 1.3. The tests were carried out by the usual method, with the apparatus shown schematically in Fig. 1.

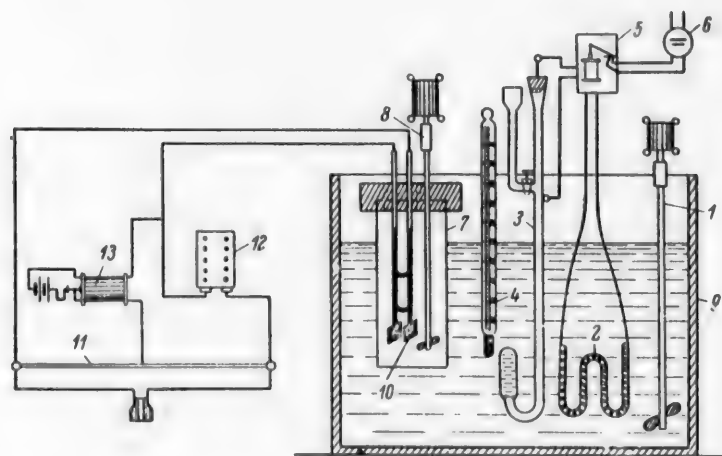


Fig. 1. Schematic design of apparatus for determination of the electrical conductivity of alkali-silicate solutions. 1) Thermostat stirrer; 2) heater; 3) toluene thermoregulator; 4) thermometer; 5) relay; 6) alternating-current source; 7) glass vessel of accurately known capacity; 8) stirrer; 9) thermostat; 10) electrodes; 11) slide wire and microphone; 12) resistance box; 13) Ruhmkorff coil.

The results of the conductivity determinations for solutions of sodium and potassium silicates, and OS-Na and OS-K, are plotted in Fig. 2. It is seen that the conductivity of the potassium silicate was considerably higher than that of the sodium silicates. Solutions of organosilicon silicates had lower conductivities than the original alkali silicates; therefore they are better insulators than water glasses.

**Fields of application of alkali organosilicon silicates.** Organosilicon silicates can be used successfully as binders in the production of articles from refractory oxides such as Al<sub>2</sub>O<sub>3</sub>, MgO, BeO, TiO<sub>2</sub>, ZrO<sub>2</sub>, and in various heat-resistant luting materials and cements.

For these purposes, OS is introduced either in powder form as a batch component, followed by mixing with water, or as 50-60% aqueous solution in which the mass is made.

Masses based on OS with various fillers have good adhesion to various materials.

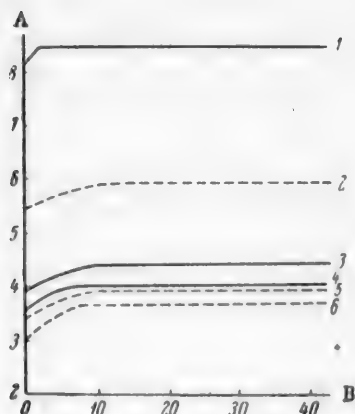


Fig. 2. Electrical conductivity of water glass (WG) and organosilicon silicates (sp.gr. 1,3). A) Conductivity (in ohm.  $\text{cm}^{-1}$ ), B) time (minutes). Curves: 1) WG-K,  $M^* = 2.0$ ; 2) OS-K,  $M = 3.0$ ; 3) WG-Na,  $M = 2.0$ ; 4) WG-Na,  $M = 2.75$ ; 5) OS-Na,  $M = 3.1$ ; 6) OS-Na,  $M = 3.3$ .

and other petroleum stores, as it is impermeable to crude or refined oil products. Gasoline was stored in a laboratory vessel with walls 5 mm thick, without loss of gasoline or destruction of the vessel.

In addition to the valuable technical qualities of OS, another great advantage that it is a solid, in lump or powder form, which makes it much simpler to transport than water glass.

#### LITERATURE CITED

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\*  $M$  = silica ratio (Translator's note).

\*\*In Russian.

According to reports from a number of organizations, OS-K with mineral fillers is successfully used as binder in the production of heat-resistant test apparatus for dynamic tests on hot parts of motors at 650-750°, at peripheral speeds of 400 meters/second.

In the building-materials industry, OS can be used as a binder for ceramic bodies, and as a drying accelerator for freshly molded ware. According to laboratory results, the drying time of raw bodies made from brick clays of the Cheremushki works is almost halved at 50° by the introduction of 5% OS.

In addition, OS may be used as a substitute for water glass in the production of acid-resistant cements and concretes, for briquetting various furnace charges, for anodic cutting of metals, for electrode coatings in electrowelding, etc.

In the casting industry, OS may be used as a core binder.

In the petroleum industry, OS may be used as lining material in the construction of concrete, brick,

# INFLUENCE OF THE COMPOSITION AND AMOUNT OF FILLER ON THE OXIDATIVE ROASTING OF FURNACE CHARGES IN DICHROMATE PRODUCTION\*

T. D. Averbukh, M. A. Serebrennikova, and N. D. Maslova

The preceding communication [1] dealt with the influence of additions to chromite ore on the oxidative roasting of furnace charges in dichromate production. The filler containing calcium oxide has a very important influence on the roasting process. It is added to the charge in order to prevent loss of soda in neutralization of the acidic oxides in chromite, and as an inert framework which makes the mass loose and allows access of oxygen to the reactive surface of the chromite grains. This dual role — chemical and physical — of the filler has been known for a long time [2,3].

Popova [3] studied the influence of the amount of calcium oxide in the roasting of lime — soda charges.

The replacement of manually-fed hearth furnaces by tubular kilns necessitated the replacement of a pure lime filler by a combined lime — magnesia filler, dolomite, or by a mixture of lime and the leached ground mass, as a lime charge yields compact beads, with decreased oxidation of the chromite, in rotary kilns.

The influence of different proportions of CaO and MgO on the roasting of the charge was studied by Doerner [4]. Vol'f and Pinaevskaia [5] studied the roasting of charges with different dolomite and magnesia contents. Chirkov [6] studied the roasting of charges containing from 11 to 19%  $\text{Cr}_2\text{O}_3$  and 40-160% of the theoretical quantity of soda; the fillers used were CaO, MgO, and mixtures of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . The effect of the composition of the filler component on the yield of soluble chromates was studied, and the results were used to formulate "rational charges" for different ores.

Further studies of the amount of filler were carried out in the Urals Chemical Sci.-Res. Institute by Magarshak and Baranova, and by Khaidukov and Pudovkina [7]. The former workers studied the roasting of charges containing 12-20%  $\text{Cr}_2\text{O}_3$  with a combined filler consisting of dolomite, limestone, CaO, and MgO. The molar ratio  $\frac{\text{CaO}}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{SiO}_2}$  ("lime modulus") was varied in the 0.28-3.31 range, and the minimum modulus necessary was found to be 2.

Khaidukov and Pudovkina studied the roasting of charges with 13-17.5%  $\text{Cr}_2\text{O}_3$ , with a combined filler consisting of dolomite with  $\text{CaCO}_3$  or  $\text{MgCO}_3$ .

On the basis of the probable mineral composition of an "equilibrium" clinker, they derived a formula for the calculation of the minimum amount of calcium oxide in the charge necessary to bind the acidic oxides in the charge, with a theoretical soda content [7].

$$\text{CaO} = 2\text{SiO}_2 + 2.33\text{Fe}_2\text{O}_3 + 1.67\text{Al}_2\text{O}_3 \text{ (in moles).}$$

\* Communication II in the series of studies of the oxidative roasting of furnace charges in dichromate production.

However, this formula does not reflect the influence of the physical structure of the clinker, and is therefore not sufficient for calculation of the optimum amount of filler and hence of the total  $\text{Cr}_2\text{O}_3$  content of the charge, which at present have to be found empirically.

All the laboratory investigations considered above were performed with gram samples in boats, with visual evaluation of the structure and hardness of the clinkers. As an approximation to factory kiln operation under laboratory conditions, we carried out experiments on the roasting of charges with fillers varying in composition and amount, not only in boats but also in the model rotary kiln described earlier [1].

### Starting Materials and Method

The results of chemical and sieve analyses of the chromite and dolomite are given in Table 1 and 2.

TABLE 1

Chemical Analysis of Chromite and Dolomite (%)

Material	$\text{Cr}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{MgO}$	$\text{CaO}$	Calcination loss	Total
Chromite № 1 . .	55.74	17.40	7.98	3.40	14.48	1.10	2.08	102.18
Chromite № 2 . .	58.75	18.60	4.85	5.47	14.90	2.02	2.28	101.87
Chromite № 3 . .	50.25	12.88	9.55	7.66	17.26	0.88	3.84	102.82
			$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$					
Dolomite № 1 . .	—	—	0.87	0.44	18.43	34.11	46.80	100.15
Dolomite № 2 . .	—	—	0.66	0.40	18.57	33.57	46.80	100.00
					(by difference)			
Dolomite № 4 . .	—	—	1.16	3.71	20.67	27.99	Not determined	—

TABLE 2

Sieve Analyses of Chromite and Dolomite (%)

Material	% retained by sieve with hole size (mm)						% passed through sieve hole size (mm)		Total
	0.15	0.12	0.10	0.088	0.067	0.06	0.067	0.06	
Chromite № 1 . .	0.97	—	4.13	5.92	35.19	—	53.55	—	99.16
Chromite № 2 . .	3.14	—	4.59	5.41	37.23	—	48.81	—	99.18
Chromite № 3 . .	—	1.37	0.73	2.46	—	31.75	—	63.69	100.00
Dolomite № 1 . .	23.25	—	14.44	16.37	32.12	—	13.12	—	99.30
Dolomite № 2 . .	—	—	8.27	26.51	—	33.51	—	31.71	100.00
Dolomite № 4 . .	—	2.96	7.43	9.70	—	37.31	—	42.60	100.00

The fillers used in partial and total replacement of dolomite were reactive oxides and carbonates of calcium and magnesium (analytical reagent grade). Soda ash, previously calcined, contained 99.5%  $\text{Na}_2\text{CO}_3$ . Dolomite No. 1 and the soda ash were sifted through a sieve with 0.12 mm holes before the charge were mixed.

All the components of the charge were thoroughly mixed in a porcelain mortar or basin. The amount of soda ash was stoichiometrically equivalent to the  $\text{Cr}_2\text{O}_3$  in all the experiments.

The method used for the oxidative roasting in boats in a model kiln was described previously [1].

# RESULTS AND DISCUSSION

Experiments in a stationary tube furnace (in boats). The furnace temperature was gradually raised from 600 to 1150° during 2 hours. The heating times were 30 minutes from 600 to 800°, and from 800 to 1000°, and 60 minutes from 1000 to 1150°.

TABLE 3

Effect of Replacement of Dolomite by Calcium Oxide

Experiment No.	Serial numbers of		Cr <sub>2</sub> O <sub>3</sub> content of charge (%)	Replacement of dolomite by CaO (%)	Amount of CaO (% of calculated)	Total Cr <sub>2</sub> O <sub>3</sub> in clinker (%)	Degree of oxidation of clinker (%)	Notes
	chromite	dolomite						
1	1	1	16	0	200	29.8	99.0	Replacement of dolomite by calcium oxide makes the clinkers more compact and strong (less friable)
17				25	304	27.9	98.6	
18				50	408	26.0	99.0	
19				75	513	24.5	98.5	
20				100	617	23.1	97.9	
2	1	1	18	0	154	32.6	99.2	25 and 50% replacement of dolomite by calcium oxide resulted in the formation of a yellow crust up to 0.1-0.2 mm thick on the clinker surface
21				25	233	30.6	98.4	
23				50	313	28.9	98.9	
24				75	393	27.5	99.1	
25				100	472	26.0	99.6	
3	1	1	20	0	117	35.2	99.5	
29				25	178	33.3	99.1	
30				50	239	31.9	97.5	
31				75	300	30.2	99.2	
32				100	361	28.9	99.1	
61	3	1	16	0	142	29.0	98.8	Clinkers stronger than from charges with No. 1 ore
63				25	216	26.8	98.8	
64				50	289	25.3	98.8	
65				75	363	24.3	97.6	
66				100	437	22.7	98.5	
62	3	1	20	0	79	33.8	95.0	Percentage oxidation 86.6, 84.3, 83.6 in different experiments
67				25	121	32.2	99.6	
68				50	162	30.7	84.8	
69				75	203	29.7	98.7	
70				100	245	28.6	98.9	
118	3	2	20	25	119	31.9	99.8	
119				50	161	30.4	95.0	
120				75	203	29.6	99.5	
123	2	4	16	0	114	28.0	95.2	
121			17.6	0	93	30.2	91.5	
110			20	0	67	32.9	86.6	
122			20	18	101	32.3	96.5	
125			20	25	133	31.6	94.8	
126			20	50	200	30.5	85.3	

The results of roasting experiments on charges with dolomite partially or totally replaced by calcium or magnesium oxides or carbonates are given in Tables 3-6. The results for a pure dolomite charge are also given. The data in the table are average results from 2-3 experiments.

The percentage CaO of the theoretical amount (from the Urals Chemical Sci.-Res. Inst. formula) was calculated with an allowance for the content of active calcium oxide in the dolomite.

The data in Table 3 show that increase of the  $\text{Cr}_2\text{O}_3$  content of the charge from 16 to 20% has no influence on the oxidation as long as enough  $\text{CaO}$  to neutralize the acidic oxides is present in the charge. The percentage oxidation decreases if there is a deficiency of calcium oxide (Experiments Nos. 62, 121, 110). The same was found subsequently for charges of different composition.

Partial and total replacement of dolomite by calcium oxide did not, as a rule, influence the degree of oxidation. However, with a 20%  $\text{Cr}_2\text{O}_3$  content, and 50% replacement of dolomite by calcium oxide, in some experiments there was a fairly sharp decrease of the percentage oxidation - from 98-99 to 85 (Experiments Nos. 68 and 126)\*.

It follows from Table 1 that in the case of chromite No. 1 replacement of dolomite, by 50% and over of calcium carbonate results in fusion and separation of the melts. In the case of chromite No. 3, 50% replacement of dolomite by calcium carbonate did not lead to fusion. An interesting fact is that the fused sinters, clearly unsuitable in modern practice, had a high degree of oxidation when roasted in thin layers under static conditions\*\*.

TABLE 4

Effect of Replacement of Dolomite by Calcium Carbonate

Experiment No.	Serial numbers of		$\text{Cr}_2\text{O}_3$ content of charges (%)	Replacement of dolomite by $\text{CaCO}_3$ (%)	Amount of $\text{CaO}$ (% of calculated)	Total $\text{Cr}_2\text{O}_3$ in clinker (%)	Degree of oxidation of clinker (%)	Notes
	chromite	dolomite						
1	1	1	16	0	200	29.8	99.0	Melt, phase separation
11				25	237	29.9	99.3	
12				50	273	29.6	98.2	
13				75	309	29.3	99.1	
14	1	—	16	100	346	29.4	98.9	
2	1	1	18	0	154	32.6	99.2	
15				25	181	32.7	99.0	
8	1	1	20	0	117	35.2	99.5	
16				25	138	35.1	99.0	
61	3	1	16	0	142	29.0	98.8	Very dense and strong clinkers. Yellow crust 0.2-0.5 mm thick formed on clinker surface
70				25	168	29.0	97.8	
72				50	193	29.0	98.1	
62	3	1	20	0	79	33.8	95.0	
73				25	94	33.9	98.0	
74				50	108	33.7	98.7	

The higher content of liquid phase in experiments in which dolomite was replaced by calcium carbonate is the consequence of the formation of a carbonate eutectic [9].

It follows from the data in Table 5 that, at the temperatures used for chromite roasting, magnesium oxide has low activity, and is almost an inert filler. Magnesia clinkers are less dense and hard than the others. Therefore the replacement of a small proportion of the dolomite (up to 25%) by caustic magnesite may be desirable.

\* Similar anomalous behavior on addition of  $\text{CaO}$  was observed by Vol'f and Popova [8] in charges containing ferric oxide filler. These charges did not sinter at  $1100^\circ$  even with soda in 30% excess over the theoretical quantity; if the excess soda was replaced by an equivalent quantity of lime, the mass sintered with 21.8% total  $\text{Cr}_2\text{O}_3$  content, and with 26% total  $\text{Cr}_2\text{O}_3$  it even fused. Thus, the replacement of soda by an infusible filler resulted in sintering and fusion.

\*\* The oxidation was probably completed before total fusion.

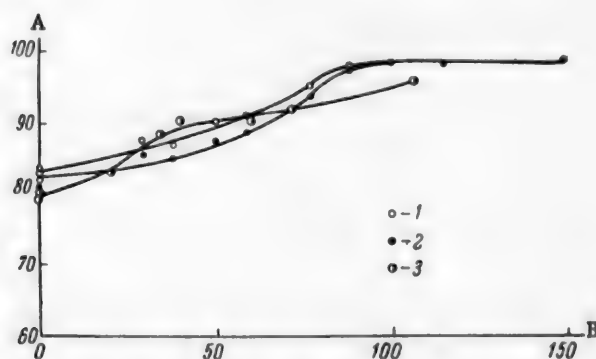


Comparison of Tables 5 and 6 (also see the diagram) shows that the degree of oxidation depends on the amount of CaO in the same way in dolomite - magnesite and dolomite - magnesia charges. Both these types of charges are also characterized by low contents of acid-soluble  $\text{Cr}_2\text{O}_3$  in the clinkers, below 0.1% (in the clinkers from the other charges studied it varied between 0.2 and 0.9%).

TABLE 5

Effect of Replacement of Dolomite by Magnesium Oxide

Experiment No.	Serial numbers of		$\text{Cr}_2\text{O}_3$ content of charge (%)	Replacement of dolomite by $\text{MgO}$ (%)	Amount of CaO (% of calculated)	Total $\text{Cr}_2\text{O}_3$ in clinker (%)	Degree of oxidation clinker (%)	Notes
	chromite	dolomite						
1	1	1	16	0	200	29.8	99.0	Loose clinkers which become denser with increase of the $\text{Cr}_2\text{O}_3$ content
33				25	150	28.1	99.0	
34				50	100	26.2	99.3	
35				75	50	24.9	90.1	
36				100	0	23.5	82.8	
2	1	1	18	0	154	32.6	99.2	Color of clinkers changes from green to yellow with increasing $\text{MgO}$ content
37				25	115	30.7	98.5	
38				50	77	29.2	95.4	
39				75	38	27.8	87.3	
40	1	—	18	100	0	26.8	81.8	
3	1	1	20	0	117	35.2	99.5	
41				25	88	33.2	98.2	
42				50	59	31.8	91.2	
43				75	29	30.4	87.5	
44	1	—	20	100	0	29.5	83.6	



Effect of CaO content on the degree of oxidation of  $\text{Cr}_2\text{O}_3$  in the roasting of dolomite - magnesite and dolomite - magnesia charges. A) Degree of oxidation of  $\text{Cr}_2\text{O}_3$  (%), B) CaO content as % of the theoretically calculated quantity. Curves: 1) Dolomite - magnesia charge, chromite No. 1; 2) dolomite - magnesite charge, chromite No. 1; 3) dolomite - magnesite charge, chromite No. 3.

#### Experiments in a Model Rotary Batch Kiln

Table 7 contains the results obtained in the roasting of dolomite, dolomite - lime, and lime charges for 2.5 hours under temperature conditions similar to those in works kilns; the temperature was raised during 1 hour to 700°, and during 30-minute intervals from 700 to 850°, from 850 to 1000°, and from 1000° to 1150°.



In some of the experiments the charge was held at 1000° for 30 minutes instead of increasing the temperature from 1000 to 1150°.

TABLE 6

Effect of Replacement of Dolomite by Magnesium Carbonate

Experiment No.	Serial numbers of		Cr <sub>2</sub> O <sub>3</sub> content of charge (%)	Replacement of dolomite by MgCO <sub>3</sub> (%)	Amount of CaO (% of calculated)	Total CrO <sub>3</sub> in clinker (%)	Degree of oxidation of clinker (%)	Notes
	chromite	dolomite						
1	1	1	16	0	200	29.8	99.0	Clinkers looser and weaker than in the replacement of dolomite by calcium oxide or carbonate
49				25	150	30.5	98.9	
50				50	100	31.0	98.7	
51				75	50	32.1	87.6	
52	1	—	16	100	0	32.7	82.8	
2	1	1	18	0	154	32.6	99.2	Color changes from dark green to pale yellow with increasing MgCO <sub>3</sub> content
53				25	115	33.4	98.1	
54				50	77	34.1	93.6	
55				75	38	34.9	85.3	
56	1	—	18	100	0	35.6	82.1	
3	1	1	20	0	117	35.2	99.5	
57				25	88	34.8	97.8	
58				50	59	36.5	88.9	
59				75	29	36.8	85.4	
60	1	—	20	100	0	37.3	83.2	
61	3	1	16	0	142	29.0	98.8	
75				25	106	29.5	96.0	
76				50	71	30.3	91.9	
77				75	35	30.8	88.0	
78	3	—	16	100	0	31.6	80.6	
62	3	1	20	0	79	33.8	95.0	
79				25	60	34.4	90.7	
80				50	40	34.4	90.0	
81				75	20	35.6	83.8	
82	3	—	20	100	0	35.9	79.2	

It follows from Table 7 that increase of the Cr<sub>2</sub>O<sub>3</sub> content from 16 to 20% appreciably decreases the degree of oxidation in roasting at 1150°. The probable explanation is that the porosity of the clinker decreases on simultaneous increase of the Cr<sub>2</sub>O<sub>3</sub> content to 20% and of the temperature to 1150°.

In all the experiments the mass partially adhered to the fireclay furnace lining. The 650-800° range is dangerous; in this range the mass tends to adhere and form beads, as the result of liquid phase formation.

Partial or total replacement of dolomite by lime did not have an adverse effect on the degree of oxidation under the model-kiln conditions. In contrast to the experiments in boats, 50% replacement of dolomite by calcium oxide at 20% CrO<sub>3</sub> content was not accompanied by a decreased degree of oxidation. If the CaO is insufficient to bind the acidic oxides, the degree of oxidation correspondingly diminishes (Experiments Nos. 70a and 70b).

The beads formed were between 2 and 30 mm in size. Comparative analyses of the beads and of the mass adhering to the lining showed that the beads had a lower chromium content and usually a higher degree of oxidation. Special investigations are needed to explain this effect, which was observed in all the model-kiln experiments with a great variety of charges.

The results obtained by the roasting of charges with partial replacement of dolomite by calcium carbonate, and by magnesium oxide and carbonate, are given in Tables 8 and 9.

TABLE 7

Effects of Total Chrome Content and Replacement of Dolomite by Calcium Oxide

Experiment No.	Serial num- bers of		Cr <sub>2</sub> O <sub>3</sub> content of charge (%)	Replacement of dolomite by CaO (%)	Amount of CaO (% of calculated)	Weight of charge (g)	Final temperature (°C)	Clinker		
	chromite	dolomite						type*	total Cr <sub>2</sub> O <sub>3</sub> content (%)	degree of oxidation (%)
49	1	1	16	0	200	510	1150	On lining. Beads	30.5 27.7	97.6 99.2
7			16	50	408	250	1000	On lining Beads	28.3 23.8	96.9 98.0
43a			20	0	117	525	1150	On lining Beads	34.4 30.9	93.6 96.5
44			20	50	239	402	1150	On lining	31.9	96.4
9 and 9a			20	50	239	200	1000	On lining Beads	29.7 ** 27.7 **	96.8 99.4
65	2	1	20	50	220	385	1150	On lining Beads	26.0 ** 31.7	95.1 98.3
45	1	—	20	100	361	420	1150	On lining Beads	29.5 27.0	97.3 97.7
68	3	1	16	0	142	442	1150	On lining Beads	30.6 27.0	96.5 99.0
12		—	16	100	437	200	1000	On lining Beads	24.1 21.7	95.2 93.5
64		1	20	0	79	378	1150	On lining Beads	28.7 ** 26.6	94.5 96.3
66	3	1	20	50	162	367	1150	On lining Beads	28.8 ** 31.2	94.0 98.0
39		—	20	100	245	317	1150	On lining Beads	29.7 25.1	96.8 99.7
70a and 70bb	2	4	20	0	67	401	1150	On lining Beads	29.2 19.7	82.3 71.6
79				18	101	406	1150	On lining Beads	29.9 27.6	88.8 95.4
79a				13	101	405	1150	On lining Beads	32.1 27.2	90.5 95.8
82				50	200	304	1150	On lining Beads	27.2 ** 29.6	96.0 98.7

\* The beads and the mass remaining on the lining at the end of the roasting were analyzed separately.

\*\* Sample probably contaminated with fireclay (during removal from lining).

The data in Table 8 show that charges in which 50% of the dolomite has been replaced by calcium carbonate (with chromite No. 3, and total chromic oxide 16%), or even only 25% (with chromite No. 1 and total chromic oxide 20%) are unsuitable because of fusion. These charges did not fuse when roasted in boats.

25% replacement of dolomite by magnesium oxide, with 20% total chromic oxide content, had a favorable effect on the physical structure of the clinker, and when this charge was roasted at 1150° the degree of oxidation was the same as in the corresponding pure dolomite charge; when roasted at 1000°, the dolomite-magnesia charge had a lower degree of oxidation than the dolomite (78.7 and 95.0 respectively).

TABLE 8

Roasting in a Model Rotary Kiln; Replacement of Dolomite by Calcium Carbonate

Experiment No.	Serial number of		Cr <sub>2</sub> O <sub>3</sub> content of charge (%)	Replacement of dolomite by CaCO <sub>3</sub> (%)	Amount of CaO (% of calculated)	Weight of charge (g)	Final temperature (°)	Clinker		
	chromite	dolomite						type	total CrO <sub>3</sub> content (%)	degree of oxidation (%)
2 and 2a	1	1	16	25	237	250	1000	On lining	29.2	93.9
33			20	25	198	468	1000	Beads	25.8	97.7
								Beads *	34.6	50.4
46 and 47	3	1	16	25	168	462	1150	On lining	30.6	98.0
								Beads	26.9	98.9
50			20	25	94	495	1150	On lining	32.6	92.7
36 and 37			16	50	193	200-400	1000	Beads	28.0	96.0
								Beads **	28.2	71.9

TABLE 9

Roasting in a Model Rotary Kiln; 25% Replacement of Dolomite by Magnesium Oxide and Carbonate

Experiment No.	Serial numbers of		Cr <sub>2</sub> O <sub>3</sub> content of charge (%)	Dolomite replaced by	Amount of CaO (% of calculated)	Weight of charge (g)	Final temperature (°)	Clinker		
	chromite	dolomite						type	total CrO <sub>3</sub> content (%)	degree of oxidation (%)
31	1	1	20	MgO	88	400	1000	On lining	33.2	78.7
40				MgO	88	400	1150	On lining	32.5	95.1
67				MgCO <sub>3</sub>	60	324	1150	On lining	31.8	92.2
	3	1	20	MgCO <sub>3</sub>	60	200	1150	Beads	20.0	82.8
21								On lining	30.8	91.9
35								On lining	32.8	80.2
						365	1000	Beads	30.1	83.5

With 25% replacement of dolomite by magnesium carbonate, with a total chromic oxide content of 20%, the oxidation was the same in the model kiln as in boats. However, an interesting effect was observed in the model kiln: the mass was strongly sintered to the lining after roasting at 1150°. This indicates an increased tendency to crust formation when dolomite is replaced by magnesium carbonate; this is an unexpected effect.

• At 700° the mass stuck to the sampler. At 700-750° the beads were "wet," and "boiled" on the surface (liberation of CO<sub>2</sub>); at 800° the beads appeared dry, but nearly all stuck to the lining. On further increase of temperature the beads dropped off the lining.

•• Surface-fused beads 10-20 mm in size with 200 g charge, and 25-30 mm with 400 g charge.

••• Mass very easily detached from lining.

•••• Mass strongly sintered to the lining at temperatures above 1000-1050°.

## SUMMARY

1. It was found that increase of the  $\text{Cr}_2\text{O}_3$  content in the charge from 16 to 20% in experiments in a model rotary kiln appreciably decreases the degree of oxidation.
2. Partial replacement of dolomite by magnesium oxide or carbonate has no effect on the degree of oxidation so long as enough calcium oxide is present to bind the acidic oxides.
3. With 25-50% replacement of dolomite by calcium carbonate the mass fuses, and forms beads of a low degree of oxidation (50-70%) in the model kiln.
4. All the powdered charges studied showed some tendency to crust and bead formation in the temperature range of about 650-800° and during the subsequent roasting. The tendency to crust formation increases with increasing  $\text{Cr}_2\text{O}_3$  content, and decreases on addition of magnesium oxide. Replacement of dolomite by magnesium carbonate unexpectedly increased the tendency to crust formation. The tendency of lime charges to form beads, known from works experience, was also observed in the model kiln, but was not so pronounced.

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# THEORETICAL ANALYSIS AND CALCULATIONS RELATING TO THE OXIDATION OF BROMIDE IONS BY CHLORINE IN THE PRODUCTION OF BROMINE BY THE BLOWING-OUT PROCESS

D. S. Stasinevich

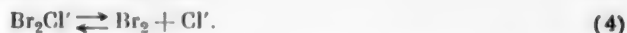
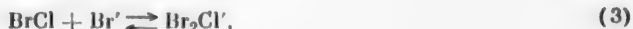
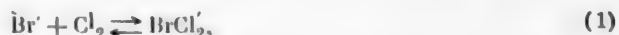
The blowing-out process is at present the main method for the production of bromine in the Soviet Union and abroad. It is carried out as follows. Brine with a relatively low bromide content (from 0.065 to 4.5 kg/m<sup>3</sup>) is treated with gaseous chlorine to liberate elemental bromine. The latter is blown out with air and absorbed in some chemical absorbent (moist iron fillings, or solutions of sodium carbonate, caustic soda, or sulfurous acid).

It is found in practice that complete oxidation of the bromide by chlorine is not effected even if an excess of chlorine is used. Bromine losses in the form of incompletely oxidized bromide comprise 10-25%, and the product contains a considerable amount of chlorine (up to 5% by weight). This creates considerable difficulties in the conversion of the iron bromide into the required bromine compounds, and necessitates the introduction of an additional stage into the process - removal of chlorine from the bromine - air mixture. The incompleteness of the oxidation of bromide by chlorine in concentrated chloride solutions is due to the equilibria  $2Br^- + Cl_2 \rightleftharpoons Br_2 + 2Cl^-$  and  $Br_2 + Cl_2 \rightleftharpoons 2BrCl$ .

The oxidation of bromide by chlorine can be considered to occur in three consecutive stages.

In the first stage the gaseous chlorine dissolves in the solution containing bromide ions. This process was studied by Pozin et al. [1].

The second stage consists of interaction of the dissolved chlorine with bromide ions; it can be represented as the following reaction sequence:



These ionic reactions proceed at high rates, and equilibrium is established almost instantaneously. Any processes involving the removal of bromine and chlorine from the equilibrium mixture must disturb the established equilibrium.

The direction in which the equilibrium is shifted depends on the relative removal rates of bromine and chlorine from the solution. It has been shown that chlorine is present in chlorinated brines mainly in the form of bromine chloride, which is more soluble in brines than elemental bromine [2]. Therefore the chlorine - bromine ratio is lower in the halogen mixture removed from chlorinated brine than in the brine itself, and the solution becomes richer in chlorine as the stripping proceeds. This creates favorable conditions for continued oxidation of bromide. Thus, the last stage of oxidation of bromide by chlorine takes place during the blowing-out of the bromine, and therefore the final results of the process can be determined only after the bromine has been blown out.

The process can be theoretically analyzed and calculated on the basis of equilibrium data for the reaction  $2Br^- + Cl_2 \rightleftharpoons Br_2 + 2Cl^-$ , and on the distribution of bromine and chlorine between the gas and liquid phases in the system  $Br_2 - Cl_2 -$  brine, contained in the preceding communication [2].

The equilibrium constant for the reaction  $2\text{Br}^+ + \text{Cl}_2 \rightleftharpoons \text{Br}_2 + 2\text{Cl}^+$  is calculated from the standard potentials of the chlorine and bromine electrodes. For convenience in calculation, both potentials should be taken for the same state, namely, the gaseous. It is then possible to avoid complex calculations of bromine and chlorine activities in solutions, and to substitute the experimentally-determined vapor pressures of bromine and chlorine over the solution into the equation for the equilibrium constant, especially as determination of vapor pressure is one of the simplest methods for determination of the activity of a dissolved substance. Moreover, data on the vapor pressures of bromine and chlorine over the solutions are used in calculations relating to the last stage of the process: completion of the bromide oxidation during the blowing-out of bromine.

The equilibrium constant for the reaction  $2\text{Br}^+ + \text{Cl}_2 \rightleftharpoons \text{Br}_2 + 2\text{Cl}^+$  at  $0^\circ$  is  $1.75 \cdot 10^{10}$ , and at  $25^\circ$   $2.2 \cdot 10^9$  and at  $40^\circ$   $8 \cdot 10^8$ . For calculation of the liquid-phase equilibrium, it is necessary to have an experimental gas phase - liquid phase composition curve for solutions of bromine and chlorine in brines of the given salt composition. If experimental curves for the given brine are not available, known curves for solutions of a similar salt composition may be used.

For calculation of the liquid-phase equilibrium, we take a series of equilibrium gas-phase compositions, and, allowing for the formation of  $\text{BrCl}$ , calculate the true  $\frac{\text{Cl}_2}{\text{Br}_2}$  ratios. Substituting these true values of the  $\frac{\text{Cl}_2}{\text{Br}_2}$  ratio for the gas phase into the equilibrium-constant equation, with the  $\text{Cl}^+$  content of the solutions known, we find the equilibrium  $\text{Br}^+$  content of the solution. We then use the curve to find the  $\frac{\text{Cl}_2}{\text{Br}_2 + \text{Cl}_2}$  ratio in the liquid phase which corresponds to the chosen  $\frac{\text{Cl}_2}{\text{Br}_2 + \text{Cl}_2}$  ratio in the gas phase, and, finally, calculate the composition of the liquid phase and the number of equivalents of chlorine needed to give the corresponding percentage oxidation. This calculation is performed for 3-4 points, and the relationship between the degree of initial bromide oxidation and the amount of chlorine fed into the given brine is thus found. The variations of the true  $\frac{\text{Cl}_2}{\text{Br}_2}$  ratio in the gas phase with the total  $\frac{\text{Cl}_2}{\text{Br}_2 + \text{Cl}_2}$  ratio calculated from the dissociation constant of bromine chloride are given below.

Variation of the True  $\text{Cl}_2/\text{Br}_2$  Ratio in the Gas Phase with the Total  $\text{Cl}_2/(\text{Br}_2 + \text{Cl}_2)$  Ratio

$\text{Cl}_2/(\text{Br}_2 + \text{Cl}_2)$ in the gas phase	0.04	0.06	0.08	0.10	0.15	0.20	0.30	0.40
True $\text{Cl}_2/\text{Br}_2$ ratios in the gas phase	0.00103	0.00215	0.00405	0.00655	0.0169	0.0394	0.124	0.362

After the equilibrium compositions of the chlorinated brine have been calculated, it is necessary to calculate the course of removal of bromine and chlorine. Exact calculation of the simultaneous removal of bromine and chlorine in a countercurrent apparatus is impossible at present. An approximate calculation procedure must therefore be used; checks have shown that this gives quite satisfactory results. The procedure is illustrated by the following example.

Initial data:  $\text{Br}^+$  concentration 270 mg/liter,  $\text{Cl}^+$  concentration 4 equiv/liter, temperature  $20^\circ$ .

The equilibrium constant for the oxidation of bromide by chlorine at  $20^\circ$  is  $3.0 \cdot 10^9$ . Data on the variations of the true  $\frac{\text{Cl}_2}{\text{Br}_2}$  ratio in the gas phase with the gas-phase composition (with bromine chloride formation taken into account), and of the liquid-phase composition with the equilibrium gas-phase composition, determined experimentally for the given brine, are used for the calculations. From these data and the equilibrium constant for the oxidation reaction (Fig. 1), we calculate the variation of the equilibrium  $\text{Br}^+$  content in the solution with the over-all composition of the gas and liquid phases for the given  $\text{Cl}^+$  concentration.

Suppose that the chlorine content in the gas phase is 8 molar % of total halogens. Then, by Fig. 1, the liquid phase contained 91 mg  $\text{Br}^+$  per liter, and  $270 - 91 = 179$  mg  $\text{Br}_2$  per liter.



By Fig. 1, the chlorine in the liquid phase is 24.5% of total halogens. Hence the chlorine content of the liquid phase is 25.8 mg/liter, and 0.88 equivalent of chlorine was used for chlorination. After calculation of the initial liquid-phase composition we proceed to calculate the course of simultaneous removal of bromine and chlorine. The composition of the initial solution (in mg/liter) is:  $\text{Br}_2$  179,  $\text{Br}'$  91,  $\text{Cl}_2$  25.8.

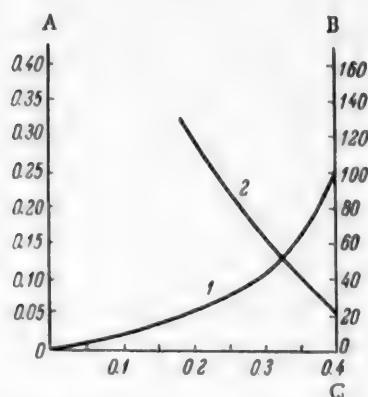


Fig. 1. Graph for calculation of the course of oxidation of bromide by chlorine, and removal of bromine and chlorine. A) Molar  $\frac{\text{Cl}_2}{\text{Br}_2 + \text{Cl}_2}$  ratio in the gas phase, Curve 1; B)  $\text{Br}'$  content of liquid phase (mg/liter), Curve 2; 3) molar  $\frac{\text{Cl}_2}{\text{Br}_2 + \text{Cl}_2}$  ratio in liquid phase.

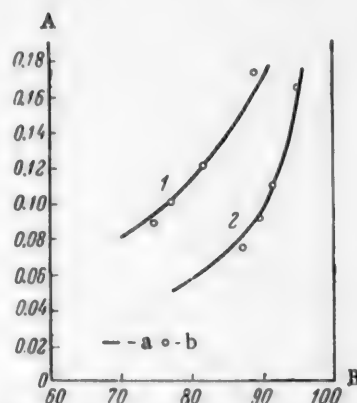


Fig. 2. Effect of the degree of oxidation of two natural brines on the chlorine content of the bromine - air mixture. A) Molar  $\frac{\text{Cl}_2}{\text{Br}_2 + \text{Cl}_2}$  ratio in the gas phase B) degree of oxidation (%). a) Calculated values, b) experimental values. Brine compositions (g/liter): 1)  $\text{Cl}'$  142,  $\text{Br}'$  0.27; 2)  $\text{Cl}'$  167,  $\text{Br}'$  0.64.

The equilibrium chlorine content of the gas phase is 8%. The first portion of the halogens blown out has the same chlorine content. Suppose that 46 mg/liter of bromine and 1.78 mg/liter of chlorine is blown out at the first stage. After this the solution contains (mg/liter):  $\text{Br}_2$  133,  $\text{Br}'$  91,  $\text{Cl}_2$  24.02. The chlorine content in the liquid phase increases to 28.9%. The amount of bromide corresponding to this chlorine content is now not 91 mg bromide per liter, but less; therefore the oxidation of bromide continues. By successive calculations we find the changed composition of the liquid phase after the first stripping stage (in mg/liter):  $\text{Br}_2$  139,  $\text{Br}'$  85,  $\text{Cl}_2$  21.35.

The equilibrium gas phase now contains 8.5% chlorine. Continued stepwise calculations for the removal of bromine and chlorine show that the total amounts blown out of the brine (in mg/liter) are:  $\text{Br}_2$  215,  $\text{Cl}_2$  9.79. The chlorine content of the bromine - air mixture should be 9.3% of the total halogens.

The spent brine contains 55 mg of unoxidized bromide per liter. The percentage oxidation of the bromide is 79.5.

The actual degree of oxidation of this brine under plant conditions is 77% with 10% of chlorine in the bromine - air mixture.

The calculated values are thus in agreement with practical data (Fig. 2).

The above method can be used to calculate the principal data required for selection of the optimum process conditions; in particular, the variation of the chlorine content in the bromine - air mixture with the degree of oxidation of the given brine, and the amount of chlorine introduced. If less than one equivalent of chlorine is fed in, its content in the bromine - air mixture is not high, but above this quantity it increases rapidly. Theoretical analysis of the process shows that the degree of oxidation can only increase up to a certain limit, corresponding to the equilibrium bromide-ion concentration for a liquid-phase composition such that the distribution coefficients of chlorine and bromine are equal. As soon as this composition is reached, further removal of bromine and chlorine proceeds without change of their ratio, and the oxidation reaction ceases. The removal of bromine and chlorine may cease either at this point, or before this point is reached,

according to the amount of chlorine used. The limiting  $\text{Br}^-$  concentration in brines of industrial importance is 4-6 mg/liter. Approximately 1.45 equivalent of chlorine is required to reach the oxidation limit. Generally oxidation is not taken as far as this, and the  $\text{Br}^-$  content of the spent brine is kept at 50-70 mg/liter; 0.85-1.0 equivalent of chlorine is used for this purpose, with up to 10 molar % chlorine in the bromine - air mixture.

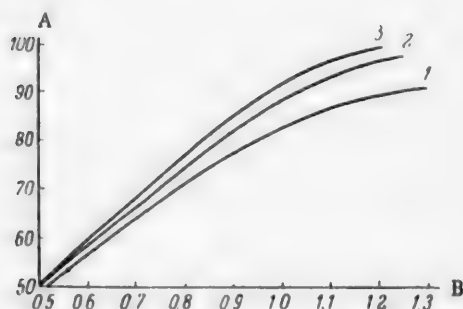


Fig. 3. Effect of chlorine feed on the degree of oxidation of bromide by chlorine at various bromide concentrations and constant chloride concentration (4 N) in the brine, at 25°. A) Degree of oxidation (%), B) amount of chlorine (equivalents). Br contents (mg/liter): 1) 160, 2) 400, 3) 800.

brine. This is shown by the following reasoning. Imagine a stripping tower in which the bromine is blown out of the brine; suppose that some definite concentration of bromide in the spent brine corresponds to the given chlorine content of the bromine - air mixture.

Consider the process below a certain cross section of the tower, i.e., the stripping of bromine from a brine with a lower bromine content. The bromine - air mixture blown out below this section has a higher chlorine - bromine ratio than at the top of the stripper. Nevertheless, both chlorine concentrations in the gas phase correspond to the same concentration of unoxidized bromide in the spent liquor; therefore, to obtain a bromine - air mixture with a given chlorine content from a brine of lower bromine concentration, less chlorine must be used for the oxidation, with more unoxidized bromide in the spent liquor.

The relationships derived above correspond to complete removal of bromine and chlorine from the brines. In actual practice the halogens are not blown out completely, because this is possible only with a large excess of air, and consequently with low efficiency of the equipment.

Theoretical analysis of the bromine process also reveals a close relationship between the oxidation and blowing stages and demonstrates that the degree of oxidation and the chlorine content of the bromine - air mixture depend not only on the oxidation conditions but also on the blowing conditions, and the percentage of removal, under constant conditions, depends to a considerable extent on the oxidation conditions.

First, attention must be drawn to the fictitious relationship between the oxidation and stripping stages; it is due to the fact that the usual method for the analysis of spent brines [3] is not adapted for analysis of equilibrium systems, and does not provide for the presence of elemental chlorine in the spent brines. In reality, bromine + chlorine is determined, rather than bromine; therefore the analytical content of free bromine is higher than the true value, while the content of unoxidized bromine, found from the difference between total bromine content and the elemental bromine content found by analysis, is less than the true value.

The desorption rate of bromine and chlorine from the solution at any point of the countercurrent apparatus is determined by the difference between their equilibrium concentration over the solution, and the actual concentration in the gas phase. If the stripping is performed at a low excess-air ratio (in equipment of appropriate dimensions), such that the amount of air is sufficient for removal of the bromine, but not for complete removal of the chlorine, then the rate of removal of chlorine by air which is already saturated to a considerable extent with chlorine must be less than in stripping with a large excess of air, when the degree of

The oxidation conditions for different brines can be compared by calculation. It follows from the reaction equilibrium  $2\text{Br}^- + \text{Cl}_2 \rightleftharpoons \text{Br}_2 + 2\text{Cl}^-$ , that for a given amount of chlorine the degree of oxidation of the bromide increases with decrease of the  $\text{Cl}^-$  concentration in the brine, increase of the bromine concentration in the brine, and decrease of temperature. This is applied both to the initial equilibrium composition of the chlorinated brine, and to the final results of the process.

Figure 3 shows the calculated relationships between the degree of oxidation and the amount of chlorine for different bromide concentrations in the brine (at constant  $\text{Cl}^-$  concentration).

The concentration of unoxidized bromine in the spent brine, corresponding to a fixed chlorine content in the bromine - air mixture, decreases with increasing concentration of bromine in the



saturation is slight. Therefore the chlorine content of the bromine-air mixture is lower at low than at high excess-air ratios.

Exact calculations relating to the simultaneous stripping of bromine and chlorine in countercurrent apparatus are not possible at present.

As stated earlier, the chlorine content of the bromine-air mixture, for a given chlorine feed, increases with increasing degree of stripping. This is illustrated in Fig. 4.

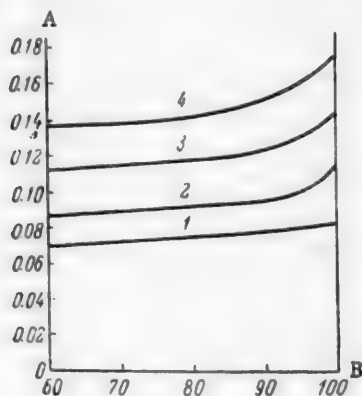


Fig. 4. Variation of the chlorine content in the bromine-air mixture with the degree of stripping for different amounts of chlorine used for  $\text{Br}_2$  oxidation. A) Molar  $\frac{\text{Cl}_2}{\text{Br}_2 + \text{Cl}_2}$  ratio in the gas phase, B) degree of stripping (%). Composition of original brine (g/liter):  $\text{Cl}^-$  142,  $\text{Br}^-$  0.27; temperature  $25^\circ$ . Chlorine consumption (equivalents): 1) 0.775, 2) 0.88, 3) 1.0, 4) 1.10.

The degree of bromine removal decreases with increase of the chlorine feed. This is because of accumulation of bromine chloride in the brine, which lowers the distribution coefficient of bromine and therefore hinders its stripping. Over-chlorination takes place, which leads to increased losses of free bromine with some decrease of bromide loss.

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## ABSORPTION OF HYDROGEN SULFIDE BY ARSENICAL SODA SOLUTION IN A FOAM APPARATUS

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The arsenical soda (Thylox) process for removal of hydrogen sulfide from gases differs from other wet processes in the value of the final product. This process yields elemental sulfur as the commercial product (and also sodium thiosulfate). The other regenerative wet processes – the sodium or potassium carbonate and the ethanolamine processes – yield gaseous hydrogen sulfide, the conversion of which into sulfur or sulfuric acid involves additional costs. However, the arsenical soda process is more complex technologically, and the equipment is more cumbersome. The absorption of hydrogen sulfide in packed towers up to 30-32 meters high involves considerable capital costs and requires high power consumption for pumping of the liquors.

It is evident that with the use of modern high-efficiency equipment for the adsorption of hydrogen sulfide in arsenical soda liquor, this process could be used more widely for removal of sulfur from various gases, and could be effected at the highest economic efficiency.

It is of interest in this connection to study the conditions for carrying out this process in foam equipment, which is highly efficient [1].

The existing studies of the arsenical soda process for hydrogen sulfide removal from gases relate mainly to the chemistry of the processes [2-5] and to determination of the reasons for the breakdown of normal operation.

Nusinov [6, 7] determined the principal process characteristics for the absorption of hydrogen sulfide in arsenical soda liquors. The experiments were performed with a solution containing 10 g  $As_2O_3$  and 14 g  $Na_2CO_3$  per liter. The initial hydrogen sulfide content of the gas was 8 g/liter, or 0.52 vol. %. At a liquor rate of 5.9 liters per  $m^3$  of gas (or about 25% excess of the reagent over the theoretical quantity), and at gas velocity of 0.55 m/second in the packed cross section, the total degree of purification was 94.5%, and the absorption coefficient was  $136 \text{ kg/m}^2 \cdot \text{hour} \cdot \text{atm}$ . It follows from the results that the absorption coefficient is independent of the hydrogen sulfide concentration, and that the spray rate has a decisive influence on the degree and rate of absorption.

Nusinov's paper also contains data on the effects of the linear gas velocity on the degree of  $H_2S$  absorption and the absorption coefficient. With increase of the linear gas velocity in the open section of the absorber from 0.5 to 1.3 m/second, the degree of absorption fell to 82%, while the absorption coefficient increased by a factor of about 1.5.

According to data at our disposal, the absorption coefficient is  $80-100 \text{ kg/m}^2 \cdot \text{hour} \cdot \text{atmosphere}$  for the absorption of hydrogen sulfide in arsenical soda liquor on the large industrial scale.

Krendel' [8] assumed that the absorption coefficient depends on the hydrogen sulfide concentration in the gas, but did not confirm this by experimental data.

It has been shown in other investigations that the rate of hydrogen sulfide absorption depends only on the hydrogen-ion concentration of the solution and the hydrogen sulfide concentration of the gas. Hydrogen sulfide is absorbed at a high rate in alkaline solutions of high pH. However, the solution is soon exhausted because of the rapid decrease of pH. The presence of arsenic, which has a buffering effect, retards the pH decrease.

Litvinenko [9] showed that in the partial-pressure range of 0.02-0.03 atm, the rate of hydrogen sulfide absorption by sodium or potassium carbonate solutions is represented by an equation [10] which is valid for processes the rate of which depends both on the concentration of the absorbent in the solution and on the partial pressure of the absorbed gas. In the region of low hydrogen sulfide pressure (below 0.02-0.03 atm) the absorption rate depends on the hydrogen sulfide partial pressure, and is almost independent of the absorbent concentration.

The characteristics of scrubbing absorption of hydrogen sulfide in arsenical soda liquors cannot be automatically applied to the absorption of  $H_2S$  in foam equipment, because of the different hydrodynamic conditions, which result in technological distinctions.

## EXPERIMENTAL •

### Apparatus, and Experimental and Analytical Procedures

The apparatus used for studies of hydrogen sulfide absorption in arsenical soda liquors in foam equipment is shown schematically in Fig. 1.

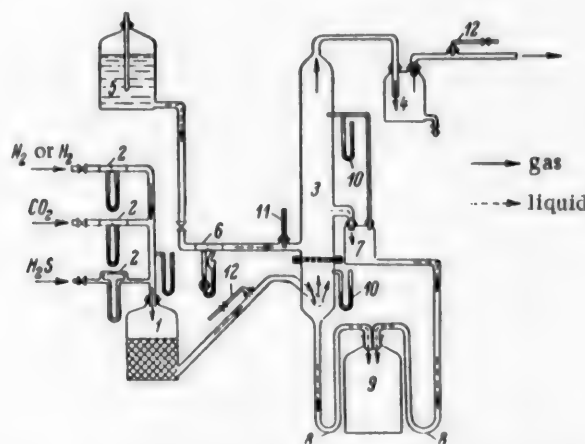


Fig. 1. Apparatus for absorption of hydrogen sulfide in foam equipment, 1) Mixer, 2) gas rheometers, 3) foam apparatus, 4) trap, 5) header, 6) liquid rheometer, 7) foam-breaking vessel, 8) hydraulic seal, 9) receiver, 10) manometer, 11) thermometer, 12) gas outlet tubes.

A gas mixture of definite composition was prepared in the mixer 1, into which the separate gases – nitrogen (or hydrogen) and carbon dioxide from cylinders, and hydrogen sulfide from a Kipp's apparatus – were fed through rheometers. From the mixer, the gas passed under the grid of the foam apparatus 3; after passing through the latter, the gas escaped into the air through the spray trap 4. The absorbent solution was fed into the foam apparatus from the vessel 5, warmed to 35-38°. The amount of liquid was varied by means of the rheometer 6. After passing through the apparatus, the liquid, in foam form, passed through the overflow orifice, the vessel 7 (for foam breaking), and the hydraulic seal 8 into the receiver 9.

Different models of the foam apparatus were described earlier [1]. Fig. 2 is a schematic diagram of the laboratory apparatus used for absorption studies. The design of the apparatus is clear from Fig. 2.

The distance of the overflow orifice from the grid level, 60 mm, determines the height of the weir which serves to support the foam on the grid. The grid is made of vinyl resin, 5 mm thick, with holes 2 mm in diameter and centers 5 mm apart. The perforated part of the grid is equal to the cross section of the apparatus, 0.0011 m<sup>2</sup>, and its open section is 15.3%.

• V. S. Bogorad took part in the experimental work

and air at 40° were passed alternately through it to convert the sodium arsenite into thioarsenite and thioarsenate. After the solution had been suitably "aged," as shown by the liberation of sulfur when air was passed through it, sodium thiosulfate was added in an amount corresponding to its content in the industrial liquor.

The arsenic content of the solution remained constant at about 6.5 g  $\text{As}_2\text{O}_3$  per liter during each experiment. The thiosulfate content rose from 200 to 210 g/liter, and the solution pH was about 8.0. If the pH fell, which was especially the case in the presence of  $\text{CO}_2$  in the gas (the pH fell by 0.1 after 1 or 2 experiments), sodium carbonate was added to keep the solution pH at 8.0.

The activity of this solution was high – the solution absorbed almost the theoretical quantity of oxygen when completely saturated with hydrogen sulfide. The regenerated solution (20 ml) did not absorb more than 0.3 ml of oxygen.

The usual methods [7, 11] were used for analysis of the solution and gas. Gas samples for analysis were collected in evacuated flasks.

The hydrogen sulfide contents of the gas at the entry and exit of the apparatus were used to calculate the tray efficiency of the apparatus (or the degree of absorption), and the absorption rate and coefficient [12, 13].

**Fig. 2. Laboratory model of a single-tray foam apparatus.** 1) Part of column above the grid, 2) part of column below the grid, 3) grid, 4) liquid inlet, 5) overflow chamber, 6) liquid overflow tube, 7) liquid drain tube, 8) liquid inlet tube, 9) gas outlet, 10) tube to manometers for pressure measurement, 11) stop hooks, 12) rubber holder.

For determination of the principal characteristics of hydrogen sulfide absorption by arsenical soda solution in the foam apparatus, and of the optimum process conditions, experiments were performed at different gas velocities in the cross section of the apparatus, and at different flow rates of the absorbent liquid. The gas velocity was varied in the range of 0.25-2.5 m/second, corresponding to variations of the gas volume rate from 1.0 to 10.2 m<sup>3</sup>/hour. The liquid feed was varied from 20 to 300 liters/hour, corresponding to flow rates from 0.67 to 10 m<sup>3</sup>/m<sup>2</sup> · hour (overflow width 0.03 m).

Figure 3 shows the variation of the absorption rate of hydrogen sulfide as a function of its partial pressure (in the concentration range from 0.0154 to 0.414 volume%).

The experiments were performed with linear gas velocity in the full section  $w = 1$  m/second and liquid rate of 75 liters/hour, or flow rate  $i = 2.5$  m<sup>3</sup>/m · hour, and at  $w = 2$  m/second and liquid rate of 150 liters/hour, i.e., at  $i = 5$  m<sup>3</sup>/m · hour. The volume ratio of liquid to gas,  $f$ , was constant at 18.75 liters/m<sup>3</sup> in both series of the experiments. The partial pressure was taken as the arithmetic mean of the partial pressures of hydrogen sulfide before and after the apparatus.

• The liquid flow rate is the ratio of the amount of liquid flowing down from the grid to the width of the overflow ( $\text{m}^3/\text{m} \cdot \text{hour}$ ).

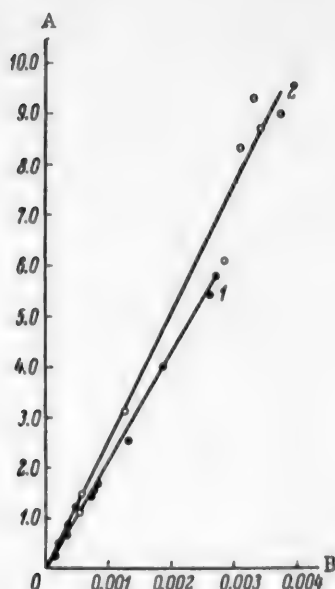


Fig. 3. Variation of the absorption rate of hydrogen sulfide with its partial pressure (at liquid-gas volume ratio of 18.75 liters per  $\text{m}^3$ ). A) Absorption rate ( $\text{kg}/\text{m}^2 \cdot \text{hour}$ ), B)  $\text{H}_2\text{S}$  partial pressure (atm). Linear gas velocity  $w$  (m/second): 1) 1, 2) 2.

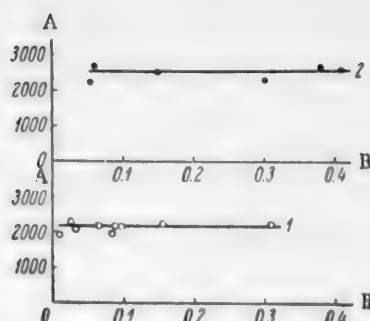


Fig. 4. Values of  $K$  for various  $\text{H}_2\text{S}$  concentrations in the gas ( $f = 18.75$  liters/ $\text{m}^3$ ). A) Absorption coefficient ( $\text{kg}/\text{m}^2 \cdot \text{hour}$ ), B)  $\text{H}_2\text{S}$  concentration in gas (volume %). Linear gas velocity  $w$  (m/second):

It follows from Fig. 3 that the absorption rate of hydrogen sulfide in the concentration range studied is directly proportional to its partial pressure  $p$  in the gas; this is in agreement with theoretical and experimental data on the absorption of other gases at low concentrations. Accordingly, the absorption rate of hydrogen sulfide by arsenical soda liquor per 1  $\text{m}^2$  of grid area can be represented by the equation

$$\frac{g}{S\tau} = K \cdot p,$$

where  $g$  is the amount of hydrogen sulfide absorbed (in kg),  $S$  is the grid area ( $\text{m}^2$ ),  $\tau$  is the absorption time (hours),  $p$  is the mean partial pressure of hydrogen sulfide in the gas (atm), and  $K$  is the absorption coefficient per 1  $\text{m}^2$  grid area (in  $\text{kg}/\text{m}^2 \cdot \text{hour} \cdot \text{atm}$ ).

Hence the absorption coefficient  $K$  can be found from the experimental data either by calculation, or graphically from Fig. 3 as the tangent of the angle between the experimental straight line and the abscissa axis. The experimental values of  $K$  fit satisfactorily on a straight line parallel to the abscissa axis in  $K - C_0$  coordinates, where  $C_0$  is the original  $\text{H}_2\text{S}$  concentration in the gas (in volume %); this shows that  $K$  is independent of the partial pressure of hydrogen sulfide in the gas (Fig. 4).

The absorption coefficient, given by the slope of the line in absorption rate - partial pressure coordinates, is  $\sim 2150 \text{ kg}/\text{m}^2 \cdot \text{hour} \cdot \text{atm}$ , at  $f = 18.75$  liters/ $\text{m}^3$  and  $w = 1$  m/second, and  $\sim 2500 \text{ kg}/\text{m}^2 \cdot \text{hour} \cdot \text{atm}$  at  $w = 2$  m/second. From the equation derived earlier [12] for the relationship between  $K$ , the tray efficiency  $\eta$  of the apparatus, and the linear gas velocity  $w$ , it follows that at constant  $K$  and  $w$  the value of  $\eta$  is also constant. In fact, as Fig. 5 shows, the efficiency of one tray at constant  $w$  is independent of the original hydrogen sulfide concentration in the gas. It is thus possible to perform calculations for multitray apparatus with the same value of the efficiency for each tray.

The table contains data on the absorption of hydrogen sulfide by arsenical soda solution in a foam apparatus, in relation to factors determining the foam regime, i.e., the linear gas velocity  $w$  (m/second) and the liquid flow rate  $l$  ( $\text{m}^3/\text{m} \cdot \text{hour}$ ). The table also includes data on the absorption capacity of the arsenical soda solution: the ratio of liquid to gas,  $f$  (liter/ $\text{m}^3$ ), and  $U$ , the excess of chemical reagent over the theoretical quantity (%). The excess of absorbent, in terms of the liquid - gas ratio  $f$ , the arsenious oxide content of the solution  $a$  (g/liter), and the amount of sulfur  $y_0$  in the gas to be purified, is given by the formula [7]

$$U = \frac{32 \cdot f \cdot a}{198 \cdot y_0} 100 - 100.$$



The variation of the tray efficiency  $\eta$  of the apparatus with  $w$  and  $i$  is shown graphically in Figs. 6 and 7.

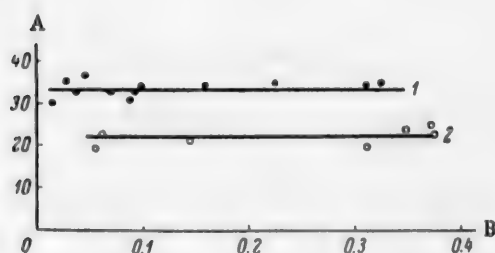


Fig. 5. Variation of tray efficiency with the original concentration of hydrogen sulfide in the gas. A) Efficiency  $\eta$  (%), B) original  $H_2S$  concentration in gas (volume %). Linear gas velocity  $w$  (m/second): 1) 1, 2) 2.

It is seen that  $\eta$  decreases steeply with increase of  $w$  and increases with increase of  $i$ . Thus, at  $i = 1.34$   $m^3$ /hour, i.e., with 40 liters of liquid fed into the apparatus per hour, the tray efficiency of the apparatus falls from  $\sim 60$  to 10% in the linear gas velocity range between 0.25 and 2.5 m/second. Increase of the liquid flow rate to 5  $m^3$ /m $\cdot$ hour (i.e., at 150 liters of liquid per hour) retards somewhat the decrease of efficiency. In this case the tray efficiency falls from  $\sim 62$  to 22% with increase of  $w$  from 0.25 to 2 m/second.

The fall of tray efficiency with increasing linear gas velocity is the result not only of a decrease of the phase contact time [14], but also of a decrease of the liquid-gas volume ratio. For a constant solution con-

centration, the amount of reagent (chemical absorbent) increases with increase of  $f$ ; by the law of mass action, this should accelerate the chemical reaction. In experiments performed at equal liquid flow rates, the ratio  $f$

Results of Experiments on the Absorption of Hydrogen Sulfide in Arsenical Soda Solution on one Tray of the Foam Apparatus ( $H_2S$  concentration in gas 0.3 vol.%; height of weir 60 mm)

Gas velocity in full section of apparatus (m/sec)	Liquid flow rate $i$ ( $m^3$ /m $\cdot$ hour)	Liquid-gas volume ratio $f$ (liter/ $m^3$ )	Excess of absorbent $U$ (% of theoretical quantity)	Tray efficiency of apparatus, $\eta$ (%)	Absorption rate $g/Sr$ (kg/ $m^2$ hour)	Absorption coefficient $K$	
						m/hour	kg/ $m^2$ of grid $\cdot$ atm $\cdot$ hr
0.25	0.67	20	420	53.3	2.06	650	985
	1.34	40	940	60.8	2.34	783	1185
	2.50	75	1850	59.1	2.23	756	1145
	5.0	150	3800	62.4	2.40	814	1235
0.5	0.67	10	160	31.2	2.34	665	1000
	1.34	20	420	38.4	3.01	868	1315
	2.50	37.5	860	43.7	3.36	1005	1520
	5.0	75	1830	55.3	4.27	1375	2035
0.75	0.67	$\sim 7$	80	19.0	2.19	567	860
	1.34	13.3	240	28.7	3.32	805	1375
	2.5	25	550	33.7	3.89	1090	1640
	5.0	50	1170	40.0	4.62	1350	2045
1.0	0.67	5	30	16.7	2.56	656	995
	1.34	10	160	20.3	3.13	810	1280
	2.5	18.75	380	32.7	5.04	1410	2140
	5.0	37.5	860	38.3	5.90	1700	2530
	7.5	56.25	1330	44.8	6.91	2075	3140
1.5	10.0	75	1830	44.6	6.86	2065	3130
	1.34	$\sim 7$	80	13.0	3.00	750	1140
	2.5	12.5	210	18.0	4.15	1070	1620
	5.0	25	550	27.0	6.22	1630	2550
2.0	7.5	37.5	860	36.2	8.30	2360	3580
	1.34	5.0	30	10.8	3.28	822	1250
	2.5	9.38	130	14.5	4.51	1130	1710
	5.0	18.75	380	22.0	6.76	1730	2700

changes very sharply with increase of the linear gas velocity. Thus, at  $i = 0.67 \text{ m}^3/\text{m} \cdot \text{hour}$   $f$  changes from 20 to 2 liters/ $\text{m}^3$  in the range of  $w$  from 0.25 to 2.5 m/second. Even at the maximum liquid flow rate ( $i = 5 \text{ m}^3/\text{m} \cdot \text{hour}$ ) the liquid-gas volume ratio at  $w = 2.5 \text{ m/second}$  is only 15 liters/ $\text{m}^3$ , i.e., below the optimum value of  $\sim 18\text{--}20 \text{ liters/m}^3$ . Evidently because of this, the absorption rate at a given liquid-flow rate increases only to a definite limit, about 1 m/second, with increase of the linear velocity (Fig. 8). Increase of the linear gas velocity from 1.0 to 1.5 m/second results in a lowering of the absorption rate at moderate liquid flow rates (1.34 and  $2.5 \text{ m}^3/\text{m} \cdot \text{hour}$ ) and to a retarded increase of the absorption rate at  $i = 5 \text{ m}^3/\text{m} \cdot \text{hour}$  (as compared with the increase in the  $w$  range up to 1 m/second). In the range of  $w$  from 1.5 to 2.5 m/second, at  $i = 1.34$  and  $2.5 \text{ m}^3/\text{m} \cdot \text{hour}$ , the absorption rate increases probably because of changes in the hydrodynamic conditions – increased turbulence of the streams, increase of foam height, etc.

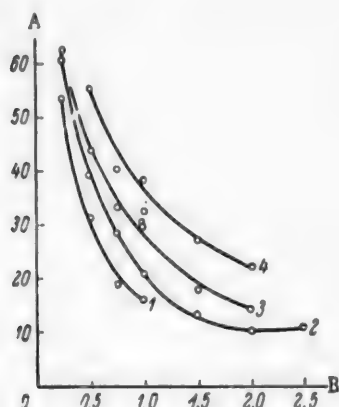


Fig. 6. Effect of linear gas velocity ( $w$ ) on tray efficiency. A) Efficiency  $\eta$  (%), B) linear gas velocity  $w$  (m/second). Flow rate  $i$  ( $\text{m}^3/\text{m} \cdot \text{hour}$ ): 1) 0.67, 2) 1.34, 3) 2.5, 4) 5.0.

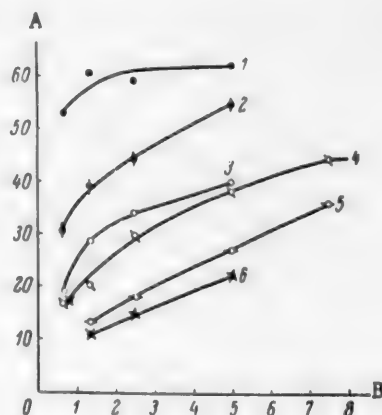


Fig. 7. Effect of liquid flow rate  $i$  on tray efficiency. A) Efficiency  $\eta$  (%), B) flow rate  $i$  ( $\text{m}^3/\text{m} \cdot \text{hour}$ ). Linear gas velocity  $w$  (m/second): 1) 0.25, 2) 0.5, 3) 0.75, 4) 1.0, 5) 1.5, 6) 2.0.

It is important to determine the effects of linear gas velocity on the absorption rate and tray efficiency at equal liquid-gas volume ratios. In this case variation of the linear gas velocity is accompanied by variations of the amount of liquid fed into the apparatus, and therefore of the liquid flow rate. As Fig. 9 shows, the absorption rate at constant  $f$  increases in proportion to the linear gas velocity. This relationship is linear at different values of  $f$  because the absorptive capacity of the solution is constant, and the slope of the lines is

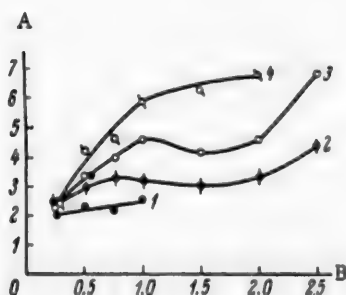


Fig. 8. Effect of  $w$  on the absorption rate of hydrogen sulfide. A) Absorption rate of hydrogen sulfide ( $\text{kg}/\text{m}^2$  of grid · hour), B) linear gas velocity (m/second). Flow rate  $i$  ( $\text{m}^3/\text{m} \cdot \text{hour}$ ): 1) 0.67, 2) 1.34, 3) 2.5, 4) 5.0.

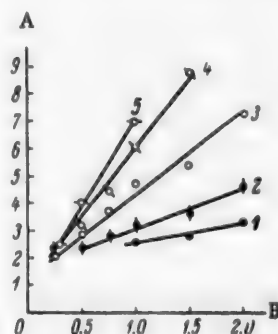


Fig. 9. Effect of  $w$  on the absorption rate of hydrogen sulfide at different values of  $f$ . A) Absorption rate of hydrogen sulfide ( $\text{kg}/\text{m}^2$  of grid · hour), B) linear gas velocity  $w$  (m/second). Values of  $f$  (liters/ $\text{m}^3$ ): 1) 5, 2) 10, 3) 20, 4) 40, 5) 75.

determined both by the absorptive capacity of the solution and by the hydrodynamic conditions at different liquid-gas volume ratios. At low values of  $f$  the absorption rate increases only slightly with increase of  $w$ ; at  $f = 20$  liters/m<sup>3</sup> the absorption rate rises steeply with increase of  $w$ . Although further increases of  $f$  to 40 and 75 liters/m<sup>3</sup> increase the absorption rate, this hardly compensates for the increased power consumption in pumping large amounts of liquid and for overcoming the increased hydraulic resistance of the apparatus.

The variations of the efficiency of a single tray in the apparatus with  $w$  at different values of  $f$  are plotted in Fig. 10.

Comparison of Figs. 6 and 10 shows that the efficiency decreases with increasing linear gas velocity much less at constant liquid-gas ratio than at constant liquid flow rate. Thus, at  $f = 20$  liters/m<sup>3</sup> the efficiency decreases approximately 1.7-fold in the range of  $w$  from 0.5 to 1.5 m/second, and at  $f = 40$  liters/m<sup>3</sup> it decreases approximately 1.2-fold. At  $i = 1.34$  m<sup>3</sup>/m<sup>3</sup> · hour, the efficiency decreases 3.2-fold in the range of  $w$  from

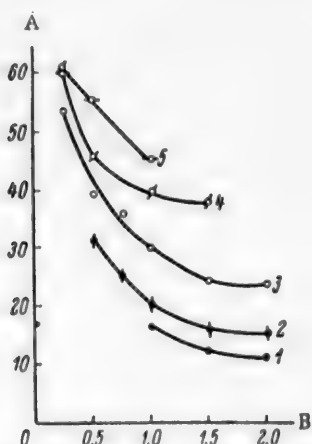


Fig. 10. Effect of  $w$  on tray efficiency at constant values of  $f$ . A) Efficiency (%), B) linear gas velocity  $w$  (m/second). Values of  $f$  (liters/m<sup>3</sup>): 1) 5, 2) 10, 3) 20, 4) 40, 5) 75.

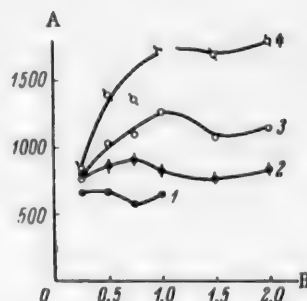


Fig. 11. Variations of  $K$  with  $w$ . A) Values of  $K$  (m/hour), B) linear gas velocity  $w$  (m/second). Flow rate  $i$  (m<sup>3</sup>/m<sup>3</sup> · hour): 1) 0.67, 2) 1.34, 3) 2.50, 4) 50.

0.5 to 1.5 m/second, while at  $i = 2.5$  m<sup>3</sup>/m<sup>3</sup> · hour it decreases roughly 3-fold. This is evidently due to the corresponding change of the absorption rate with variation of the linear gas velocity, with the liquid-volume ratio, or the liquid flow rate, constant respectively. However, the absorption coef-

ficient is more suitable than the absorption rate for characterization of the absorption process.

It was shown earlier that the absorption coefficient of hydrogen sulfide, in the concentration range studied, is constant at  $f = 18.75$  liters/m<sup>3</sup> and constant  $w$ . To determine the optimum operating conditions for the foam apparatus, it is necessary to consider the variation of  $K$  over a wider range of linear gas velocities and liquid flow rates.

Figure 11 shows that at  $i = 5$  m<sup>3</sup>/m<sup>3</sup> · hour,  $K$  increases sharply over the range of  $w$  from 0.25 to 1 m/second, and then remains virtually constant. At other values of  $i$ ,  $K$  first increases and then decreases. This shows that the resistances of the gas and liquid phases [15] differ in their influence on the absorption of hydrogen sulfide, according to the process conditions. For example, the liquid-phase resistance may be ignored only at  $i = 5$  m<sup>3</sup>/m<sup>3</sup> · hour, and in this case the absorption rate increases continuously over the entire range of linear gas velocities from 0.25 to 2 m/second, although the increase is small at  $w > 1$  m/second. At a liquid flow rate of 2.5 m<sup>3</sup>/m<sup>3</sup> · hour the liquid-phase resistance begins to have an appreciable influence on absorption, and therefore the absorption coefficient increases with increase of  $w$  only up to  $\sim 1$  m/second. When the liquid flow rate falls to 1.34 m<sup>3</sup>/m<sup>3</sup> · hour, the absorption rate is determined mainly by the liquid-phase resistance. In this case the absorption coefficient increases with  $w$  only up to 0.75-0.85 m/second. At constant liquid-gas volume ratios the absorption coefficient increases continuously with increasing linear gas velocity, but the extent of the increases depends on  $f$  (Fig. 12). Thus, at  $f = 20$ -75 liters/m<sup>3</sup>, the absorption coefficient increases sharply with  $w$ . If  $f$  is reduced to 10 or 5 liters/m<sup>3</sup>, the increase of the absorption

coefficient with the gas velocity is less rapid. This is because of the different hydrodynamic conditions of the gas-liquid system, which determine the degree of turbulence of the individual streams and the relative role of the liquid-phase resistance in the absorption process.

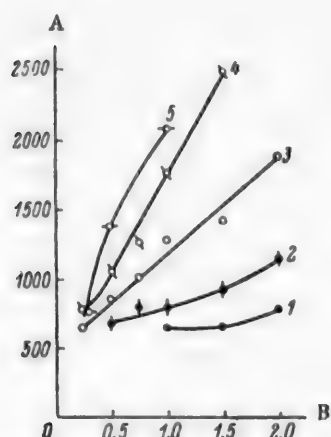


Fig. 12. Effect of  $w$  on  $K$  at constant values of  $f$ . A) Values of  $K$  (m/hour), B) linear gas velocity  $w$  (m/second). Values of  $f$  (in liters/m<sup>3</sup>): 1) 5, 2) 10, 3) 20, 4) 40, 5) 75.

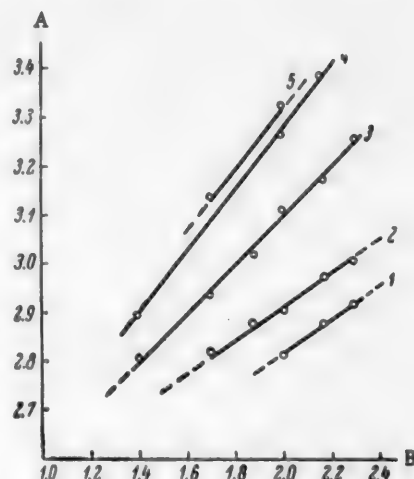


Fig. 13.  $K$  as a function of  $w$  in logarithmic coordinates: A)  $\log K$ , B)  $\log w$ . Values of  $f$  (liters/m<sup>3</sup>): 1) 5, 2) 10, 3) 20, 4) 40, 5) 75.

Figure 13, shows a logarithmic plot of  $K$  against  $w$ . It is seen that the function  $K = \phi(w)$ , plotted in logarithmic coordinates, gives straight lines of different slopes which depend on the liquid-gas volume ratio. It follows that at constant  $f$  the variation of the absorption coefficient with the linear gas velocity in the foam apparatus is represented by the equation  $K = a \cdot w^n$ . The values of  $n$ , determined from the slopes of the lines in Fig. 13, are 0.33 at  $f = 5$  and 10 liters/m<sup>3</sup>, 0.5 at  $f = 20$  liters/m<sup>3</sup>, and 0.625 at  $f = 40$  and 75 liters/m<sup>3</sup>. These results show that the liquid-phase resistance plays an important role in the absorption of hydrogen sulfide by arsenical soda solution in the foam apparatus. The relative significance of the liquid-phase resistance in the total resistance to absorption depends on the liquid-gas volume ratio. The liquid-phase resistance is greater at lower liquid-gas volume ratios, i.e., with less excess absorbent over the theoretical quantity. However, the capacity of the absorbent is very high, especially at  $f \approx 20$  liters/m<sup>3</sup>, and the driving force of absorption under these conditions (i.e., at low partial pressures of hydrogen sulfide) is essentially determined only by the partial pressure of the gas.

At the same time, the absorption rate and coefficient depend appreciably on the hydrodynamic conditions of the foam apparatus.

The absorption coefficients under foam conditions are some tens of times the coefficients of absorption of hydrogen sulfide in scrubbers. As has been stated, the absorption coefficient of H<sub>2</sub>S in scrubbers under industrial conditions does not exceed 100 kg/m<sup>3</sup> · hour · atm. The values found for the absorption coefficient of hydrogen sulfide in the foam apparatus, at  $f = 18.75$  liters/m<sup>3</sup>, are 2150 kg/m<sup>3</sup> · hour · atm, at  $w = 1$  m/second, and 2500-2700 kg/m<sup>3</sup> · hour · atm, at  $w = 2$  m/second. Even at  $w = 0.5$  m/second,  $K = 868$  kg/m<sup>3</sup> · hour · atm, (at  $f = 20$  liters/m<sup>3</sup>).

An intertray distance of 0.5 m is adequate for normal operation of the foam apparatus. It thus follows from the above results that removal of hydrogen sulfide from gases by absorption in arsenical soda liquor can be effected in the foam apparatus at about 17 times the rate attainable in scrubbers, at  $w = 0.5$  m/second, at about 40 times the rate at  $w = 1$  m/second; and at about 50 times the rate at  $w = 2$  m/second.

## SUMMARY

1. The absorption rate of hydrogen sulfide in arsenical soda solution in the foam apparatus was studied, and it was found that in the  $H_2S$  concentration range used (up to ~4 volume %), at constant liquid-gas volume ratios and linear gas velocities, the absorption coefficient and the efficiency of a single tray of the apparatus are independent of the hydrogen sulfide concentration in the gas.
2. The tray efficiency of the apparatus decreases from 55-65%, depending on the liquid flow rate, at gas velocity 0.25 m/second, to 10-20% at gas velocity 2 m/second.
3. At constant liquid-gas volume ratios, the absorption rate and coefficient are proportional to the linear gas velocity.
4. At low liquid-gas volume ratios ( $f = 5-10$  liters/ $m^3$ ) the absorption coefficient varies in proportion to the gas velocity to the power 0.33, and increases 1.2 to 1.4-fold in the range of 1 to 2 m/hour.
5. At high liquid-gas volume ratios the absorption coefficient increases approximately 2-fold in the range from 0.5 to 1.5 m/second at  $f = 20$  liters/ $m^3$ , and approximately 2.5-fold at  $f = 40$  liters/ $m^3$ ; these variations are proportional to the gas velocity to the power 0.5 and 0.66 respectively.
6. The absorption coefficients in the absorption of hydrogen sulfide in the foam apparatus, say at  $f = 18-20$  liters/ $m^3$ , are some tens of times as high as the absorption coefficients in scrubbers.
7. If foam equipment is used instead of scrubbers for sulfur removal, the volume of the absorption equipment is very much diminished.

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## VARIATION OF THE DENSITY OF PURE NITRIC ACID WITH THE TEMPERATURE

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Data on the density of pure nitric acid over a relatively wide temperature range were required in relation to a study of its thermal decomposition.

The results of density determinations on pure nitric acid at various temperatures (above 0°) have been repeatedly reported in the literature. Thus, the standard reference books [1,2] give densities for the 5-30° range. These tables are based on data published before 1927. However, more recent determinations are not in complete agreement with the data in the standard tables.

Mishchenko [3] reported in 1929 that the density of pure nitric acid is 1.54786 g/cc at 0°, and 1.5215 g/cc at 15°. Klemenc and Rupp [4], who studied the density of the system  $\text{HNO}_3 - \text{NO}_2$  at 0, 12.5, and 25°, obtained the following values for the density of pure  $\text{HNO}_3$  at these temperatures: 1.5472, 1.5245, and 1.5018 g/cc. Briner et al. [5] found in 1935 that the density of pure nitric acid at 24.9° is 1.5033 g/cc.

Several more reports on the density of pure nitric acid have been published in recent years.

Stern and Kay [6] carried out some very careful measurements and derived the following equation for the density in the 0-32° range:

$$d_t = 1.5492 - 0.00182t, \quad (1)$$

According to the authors, the accuracy of these results lies within the  $\pm 0.0001$  g/cc range.

Masson et al. [7], in a 1955 paper on the density and viscosity of the system  $\text{HNO}_3 - \text{H}_2\text{O} - \text{N}_2\text{O}_4$ , reported that the density of pure nitric acid at 0, 25 and 40° is 1.549, 1.504, and 1.477 g/cc respectively. In the same year, Sprague and Kaufman [8] stated in a paper on the density of three-component solutions of  $\text{HNO}_3 - \text{H}_2\text{O} - \text{N}_2\text{O}_4$ , that the density of pure nitric acid varies in the 35-65° range according to the equation

$$d_t = 1.48297 - 0.0018(t - 35^\circ), \quad (2)$$

In the opinion of these authors the total error is within the limits of  $\pm 0.001$  g/cc, i.e., their experimental densities are accurate to some thousandths of a unit.

The literature data indicate that the temperature coefficient of the density of pure nitric acid probably varies very little in the 0-65° range, and is in the limits of 0.00180 - 0.00182 g/cc · degree.

We were unable to find relevant data for the temperature region below 0° in the literature, and there is no certainty that extrapolation with the aid of one of the above equations is possible. Moreover, the results obtained by different authors for the density of the acid at 0° are not in satisfactory agreement.

It therefore became necessary to determine experimentally the density of pure  $\text{HNO}_3$  at various temperatures, in order to derive an equation suitable for interpolation in the range of -30 to +60°.

### EXPERIMENTAL

The density determinations were performed with the acid of a glass pycnometer, of about 10 ml capacity, specially adapted for experiments on the same sample at different temperatures. The determinations were



performed over the temperature range from  $-30$  to  $+50^{\circ}$ . Pure nitric acid was prepared by double vacuum distillation of a mixture of concentrated nitric and sulfuric acids. The product was kept at temperatures below  $50^{\circ}$ . Analyses performed before the density determinations showed that the acid contained about  $0.04\%$   $\text{NO}_2$ .

At the end of each determination, which took not more than 3 hours (with one sample), the  $\text{NO}_2$  content either increased by  $0.01$ – $0.03\%$  over the initial value, or remained almost unchanged. Therefore corrections were applied to the experimentally determined densities, based on the fact [9] that addition of  $1\%$   $\text{NO}_2$  to pure nitric acid increases the density by an average value of  $0.0035$  g/cc.

The water content of the nitric acid before and after the experiment was determined potentiometrically and was found to be almost zero (not more than a few hundredths of one per cent). The freezing point of the nitric acid was found to be  $-41.6 \pm 0.1^{\circ}$ , which is in good agreement with published data [6, 10, 11].

The probable maximum error in our measurements was largely determined by: a) error in temperature measurements, which did not exceed  $0.05^{\circ}$  in the  $0$ – $50^{\circ}$  range, giving an inaccuracy of  $0.0001$  g/cc in the value found for the density, and in the  $0$  to  $-30^{\circ}$  range the corresponding values were  $0.2^{\circ}$  and  $0.0004$  g/cc; b) error in the volume measurements, not greater than  $0.01$  cc, corresponding to about  $0.0002$  g/cc.

The total maximum error probably does not exceed  $\pm 0.0003$  g/cc for the  $0$  to  $50^{\circ}$  range, and  $\pm 0.0006$  g/cc for the  $0$  to  $-30^{\circ}$  range.

TABLE 1

Comparison of Experimental and Calculated Densities of Pure  $\text{HNO}_3$  at Various Temperatures

Temperature ( $^{\circ}$ )	Density d		$\Delta d$	Temperature ( $^{\circ}$ )	Density d		$\Delta d$
	experimental	calc. from Eq. (3)			experimental	calc. from Eq. (3)	
$-30$	1.6043	1.6042	$+0.0001$	$+10$	1.5806	1.5810	$-0.0004$
$-25$	1.5951	1.5950	$+0.0001$	$+15$	1.5220	1.5218	$+0.0002$
$-20$	1.5846	1.5858	$-0.0012$	$+20$	1.5124	1.5126	$-0.0002$
$-15$	1.5779	1.5767	$+0.0012$	$+25$	1.5034	1.5035	$-0.0001$
$-10$	1.5695	1.5676	$+0.0009$	$+30$	1.4945	1.4944	$+0.0001$
$-5$	1.5591	1.5584	$+0.0007$	$+40$	1.4770	1.4760	$+0.0010$
$\pm 0$	1.5494	1.5492	$+0.0002$	$+50$	1.4582	1.4578	$+0.0004$
$+5$	1.5397	1.5401	$-0.0004$				

## RESULTS

The results of the experimental determination of the density of pure  $\text{HNO}_3$  in the range from  $-30$  to  $+50^{\circ}$  are given in Table 1. These values are the ratios of the weights of the same volume of acid at the respective temperatures to that of water at  $-4^{\circ}$ , with corrections for weighing in air.

These experimental results are satisfactorily represented by the Equation (1) given above, in which the temperature coefficient was changed by one unit in the fifth decimal place:

$$d_t = 1.5492 - 0.00183t.$$

The observed discrepancies between the experimental and calculated values do not exceed the probable error. Hence we may conclude that the temperature coefficient of the density changes only slightly in the range from  $-30$  to  $+50^{\circ}$ , and may be taken as constant and equal to  $0.00183$  g/cc  $\cdot$  degree to the nearest unit in the fifth place.

The experimental and literature data on the density of pure nitric acid at various temperatures are compared in Table 2. Column 2 gives the experimental values smoothed by means of Equation (3). The literature data were obtained by graphical interpolation from the reported values; this presented no difficulties, as the  $d$ - $t$  plots were linear.

TABLE 2

Comparison of Experimental and Literature Data on the Density of Pure  $\text{HNO}_3$  at Various Temperatures

Temperature (°)	Density data of											
	this paper		Botti [1]		Mishchenko [3]		Klemenc and Rupp [4]		Stern and Kay [6]		Masson et al. [7]	
	d	$\Delta d$	d	$\Delta d$	d	$\Delta d$	d	$\Delta d$	d	$\Delta d$	d	$\Delta d$
0	1.5492	—	—	—	1.5479	+0.0013	1.5472	+0.0020	1.5492	0.0000	1.549	+0.0002
5	1.5401	1.5402	-0.0001	—	1.5391	+0.0010	1.5381	+0.0020	1.5401	0.0000	1.540	+0.0001
10	1.5310	1.5310	0.0000	—	1.5304	+0.0006	1.5280	+0.0020	1.5310	0.0000	1.531	—
15	1.5218	1.5217	+0.0001	—	1.5215	+0.0003	1.5200	+0.0013	1.5219	-0.0001	1.522	-0.0004
20	1.5126	1.5129	-0.0003	—	—	—	1.5109	+0.0017	1.5128	-0.0002	1.513	-0.0004
25	1.5035	1.5040	-0.0005	—	—	—	1.5018	+0.0017	1.5037	-0.0002	1.504	-0.0005
30	1.4944	1.4952	+0.0008	—	—	—	—	—	1.4946	-0.0002	1.495	-0.0006
35	1.4852	—	—	—	—	—	—	—	—	—	1.486	-0.0003
40	1.4760	—	—	—	—	—	—	—	—	—	1.474	+0.0022
45	1.4669	—	—	—	—	—	—	—	—	—	1.465	+0.0020
50	1.4578	—	—	—	—	—	—	—	—	—	1.456	+0.0019
55	1.4486	—	—	—	—	—	—	—	—	—	1.447	+0.0018
60	1.4394	—	—	—	—	—	—	—	—	—	1.438	+0.0016
65	1.4303	—	—	—	—	—	—	—	—	—	1.439	+0.0014
											1.429	+0.0013

• Extrapolated from Equation (3).

Table shows that in most cases the discrepancies do not exceed the permissible probable error.

Hence it may be concluded that Equation (3) represents the density of pure nitric acid as a function of temperature in the range from  $-30$  to  $+65^\circ$ ; the densities of pure  $\text{HNO}_3$  at various temperatures, given in Table 3, can be recommended for practical use.

TABLE 3

Recommended Values for the Density of Pure  $\text{HNO}_3$  in the  $-30$  to  $+65^\circ$  range

$t$ ( $^\circ\text{C}$ )	$d$ (g/cc)	$t$ ( $^\circ\text{C}$ )	$d$ (g/cc)	$t$ ( $^\circ\text{C}$ )	$d$ (g/cc)
$-30$	1.6042	$+5$	1.5401	$+40$	1.4760
$-25$	1.5950	$+10$	1.5310	$+45$	1.4669
$-20$	1.5858	$+15$	1.5218	$+50$	1.4578
$-15$	1.5767	$+20$	1.5126	$+55$	1.4486
$-10$	1.5676	$+25$	1.5035	$+60$	1.4394
$-5$	1.5584	$+30$	1.4944	$+65$	1.4303
$\pm 0$	1.5492	$+35$	1.4852		

#### SUMMARY

1. The density of pure nitric acid in the range of  $-30$  to  $+50^\circ$  was determined; it was found that the temperature coefficient of the density of pure  $\text{HNO}_3$  is almost constant and has the value

$$\frac{\Delta d}{\Delta t} = 0.00183 \text{ g/cc} \cdot \text{degree.}$$

2. The density of pure  $\text{HNO}_3$  as a function of the temperature is satisfactorily represented in the range of  $-30$  to  $+65^\circ$  by the linear equation

$$d_t = 1.5492 - 0.00183t.$$

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## DETERMINATION OF THE EVAPORABILITY OF OILS AND GREASES

F. K. Volynets

Lubricating oils and greases used in optical instruments (OI) must conform to special requirements determined by the special features of such instruments. One such requirement is low volatility. One reason is that volatilization of oils and greases is the cause of condensed greasy deposits on the optical surfaces [1, 2]. Further, lubricants in optical instruments must be effective for long periods at regions of friction, as it is often impossible to change the lubricant when the instrument is in use. Therefore volatilization of the more volatile components may lead to appreciable changes of viscosity, setting temperature, and other properties of the oils [3], with a consequent disturbance of the normal operation of the instrument. In the case of greases, evaporation not only alters the effective viscosity, yield value, and frost resistance, but also causes condensation and cracking of the lubricant layer, which loses its protective properties as a result [4].

The evaporation of oils and greases is also important in other application fields. Thus, in the case of engine [5] and cylinder [6] oils, which operate at high temperatures, it causes waste of oil, and in the case of compressor oils it leads to the formation of explosive mixtures. Viscosity changes in watch oils [7], caused by evaporation of volatile components, influence the accuracy of the watches; the same is true for other control and measurement instruments. Evaporability is especially important in relation to oils used in jet-engine technology [8], and oils used at high temperatures and low pressures, i.e., under conditions favoring evaporation.

The above considerations account for the recent increased interest in the evaporability of oils and greases, and methods for its determination.

Because of their simplicity and ease gravimetric methods for estimation of oil and grease evaporability are the most widely used [5, 7, 9, 10]. They essentially consist of determinations of the weight loss of a sample of oil or grease under specified conditions in a given time. In recent variations of this method, thin layers, similar to those used in practice, are used for the evaporation. The results (weight loss or the amount of oil evaporated) are expressed as percentages of the original samples, or in mg per cm<sup>2</sup> of evaporation surface.

However, the existing gravimetric methods have considerable disadvantages. Among these is the unsatisfactory reproducibility of the results [1, 8, 9]. There are two main causes of this. First, the fixed experimental conditions are usually in the temperature, evaporation area, and time. However, these parameters are insufficient to define the experimental conditions, as the evaporation rate is very strongly dependent on the vapor pressure and the intensity of the convection currents of air over the evaporation surface. These conditions are determined by such factors as the volume of the thermostat used for the test, the shape of the evaporator, and even the character of its edges [11, 12]; such "details" are usually disregarded, and the reproducibility is unsatisfactory as a result. Second, the weight losses in the existing methods are usually small, especially with oils of low volatility, and are at the sensitivity limits of the analytical balance. The use of analytical balances for determinations of the weight loss is another cause of the unsatisfactory reproducibility of the experimental results. These facts make correct selection of oils and greases, especially of similar evaporability, on the basis of the results of existing gravimetric methods, difficult.

Another important disadvantage of the existing gravimetric methods is that they only give comparative values for the evaporability of oils under specified conditions; these are inadequate for evaluation of oil

evaporability over prolonged periods under service conditions. It is thus impossible to determine the influence of evaporability on the other properties of oils and greases, and thus to determine the normal service life of a frictional region. This, however, is the critical problem in the choice of a lubricant. Finally, it should be noted that evaluation of oil and grease evaporability in terms of weight loss under specified evaporation conditions cannot be regarded as satisfactory, because it does not reflect the progressive decrease in the evaporation rates of petroleum oils and other mixtures.

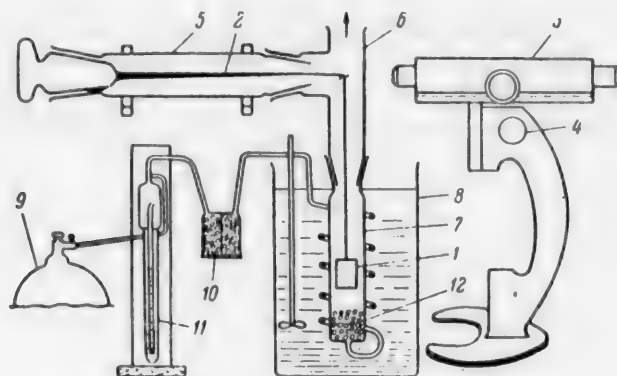


Fig. 1. Instrument for determination of the evaporability of oils and greases.

The test used by the optical-instrument industry (OI), based on the formation of a condensed oily deposit when the temperature is decreased [1] does not permit a clear differentiation between various oils and greases with regard to their evaporabilities.

A gravimetric method was also used in the present investigation for determinations of oils\* and greases\* evaporability. However, a quartz microbalance was used for determinations of the weight loss; by this means the weighing was more accurate and could be performed without interruption of the experiment. The latter factor is very important for studies of evaporation kinetics.

A diagram of the apparatus used is shown in Figure 1.

A paper or metal foil strip 1,  $20 \times 25$  mm in size, was suspended from the glass pointer 2 by means of a thin wire. The paper or foil strip was coated with 50-60 mg of oil or greases in a uniform layer  $\sim 60 \mu$  thick or less. The deflection of the pointer is directly proportional to the load. A linear calibration graph can therefore be used to find the weight of the original sample ( $g_0$ ), and its variation during the experiment, i.e., the weight loss ( $m$ ). The pointer deflection was read off with the aid of the measuring microscope 3, attached to the stand of an ordinary microscope and moved vertically by means of the rack 4. One division of the rack scale corresponded to a pointer deflection of  $2 \mu$ . With the pointers used, this deflection was equivalent to weight changes of 0.02 and 0.05 mg. The pointer was protected from fluctuations caused by air currents in the building, by means of the tube 5 and the T-piece 6. The paper or foil strip was placed in the cell 7, which was contained in the thermostatic bath 8 with the temperature constant to the nearest  $0.1^\circ$ . Nitrogen, dried in calcium chloride 10, could be blown through the cell from the cylinder 9. Nitrogen was used in order to prevent oxidation of the oil during the experiments. The nitrogen flow rate was measured by means of the rheometer 11. A layer of alumina gel 12, about 1 cm thick, was spread over the floor of the cell to insure uniform flow of nitrogen over the cross section of the cell. The grain size of the alumina gel was 1.0-1.5 mm.

Although this apparatus gives more accurate results in evaporability determinations, without interruption of the experiments, even without the use of a current of nitrogen, in this case adequate reproducibility is not obtained, as the experimental conditions remain as indefinite as in the other methods. The cell dimensions and shape also influence the reproducibility.

For example, determinations of the evaporability of OI oils at  $90^\circ$ , in absence of a current of nitrogen, in cells of different shape but of similar volume (Fig. 2), gave appreciably different results (Table 1). This is

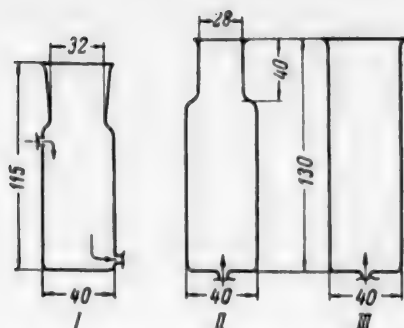


Fig. 2. Dimensions and shapes of the test cells.

because the air convection currents differ in intensity in cells of different shape. Evidence for this is provided by the fact that the bath temperature must be different in order to give the same temperature (90°) in these cells (Table 1).

Moreover, air convection currents cause temperature irregularities both across the cell and vertically. Because of this, the paper strip must be located in a strictly defined region of the cell, even when the same cell is used for all the experiments, for reproducible results. However, in this case the temperature and the velocity of the air stream over the evaporation surface, to which the experimental results should be referred, remain indefinite.

Therefore additional parameters are necessary for precise definition of the experimental conditions and for good reproducibility.

Martynov [8], who determined oil evaporability by means of similar apparatus, considers that good reproducibility can be achieved if the experiments are performed at zero oil-vapor pressure inside the cell; in his opinion the evaporation rate is then at its maximum, and good reproducibility should therefore be obtained. To obtain zero oil-vapor pressure inside the cell, he recommends the use of a current of air at a rate of 0.5-1.0 liter/hour, an adsorbent placed in the cell, or the simultaneous use of both methods.

TABLE 1

Influence of Cell Dimensions and Shape on the Experimental Results (cells without T-piece, Temperature 90°, OI oil, filter paper 20 × 25 mm)

Evaporation time (minutes)	Cell I	Cell II			Cell III		
	Bath temperature (° C)						
	95.5	94.0			102.5		
		<i>g</i>	<i>m</i>	<i>v</i> · 100	<i>g</i>	<i>m</i>	<i>v</i> · 100]
0		57.55	—	—	56.65	—	—
15		51.40	6.15	10.7	49.15	7.50	13.2
30		48.00	9.55	16.6	45.25	11.40	22.1

Note: *g* = weight of oil (mg);  $\nu \cdot 100$  = oil evaporated (%),  $\nu = \frac{m}{g_0}$ .

However, experiments performed at different nitrogen-flow rates showed that the evaporation rate begins to increase only after the current of nitrogen has reached an average velocity of 0.4 cm/second (0.3 liter per minute), as shown in Table 2. Lower nitrogen-flow rates have no effect because they are less than the velocities of the air convection currents in the cell at the given temperature. This limit evidently depends on the temperature and the cell shape and dimensions, which determine the convection intensity.

If the nitrogen flow rate is increased above 0.4 cm/second, the evaporation rate increases without any tendency to reach a limit; this is in agreement with the available data on the effect of the velocity of a gas stream over an evaporation surface on the evaporation rates of individual liquids [11]. Therefore Martynov's data, according to which a maximum evaporation rate is reached at air flow rates of 0.5-1.0 liter per hour must be regarded as erroneous. Moreover, the use of a fixed volume flow rate of air, with unspecified dimensions and shape of the cell, is inadmissible, because the experimental conditions cannot be reproduced exactly.



With regard to the use of an adsorbent in order to establish zero oil-vapor pressure in the cell, it must be pointed out that the adsorbent may have an appreciable influence on the evaporation rate at low temperatures. Vapor adsorption, and hence the influence of the adsorbent on the evaporation rate, decrease with increase of temperature; at 90° this influence should be negligible. Moreover, in absence of a current of nitrogen and at elevated temperatures the adsorbent cannot eliminate the uncertainty in the experimental conditions due to the air convection currents in the cell. Thus, the desired aim is not achieved by the use of an adsorbent alone. In the presence of a current of nitrogen the adsorption of oil vapor is possible only if its diffusion rate is greater than the velocity of the gas stream. Experiments performed specially in this connection showed that at 90° and nitrogen rate 1.38 cm/second the presence of an adsorbent (activated carbon) in the cell does not increase the evaporation rate of OI oil.

TABLE 2

Effect of Nitrogen Flow Rate on the Evaporation Rate of OI Oil (filter paper 20 × 25 mm, Cell II, cell temperature 90°)

Original weight of oil sample, mg	57.65	54.30	53.25	55.60*	53.70	55.45	56.80	58.55	56.60	58.75	56.05	56.75
Nitrogen flow rate in liters/min	0	0.03	0.30	0.53	0.645	0.81	0.935	1.15	1.275	1.385	1.510	1.605
in cm/sec.	0	0.04	0.40	0.70	0.85	1.08	1.24	1.53	1.68	1.92	2.00	2.13
Weight loss in 30 min in mg	9.50	9.40	9.40	9.95	9.75	10.10	10.30	10.70	10.85	11.10	11.00	11.25
in %	16.50	17.30	17.70	17.90	18.20	18.20	18.10	18.30	19.20	18.90	19.60	19.80

\* Experimental temperature 90.2°.

TABLE 3

Evaporation Kinetics of Amylnaphthalene from Filter Paper and Brass Gauze (Evaporation area 10 cm<sup>2</sup>, temperature 90°, time between successive readings (Δt) 5 minutes)

Evaporation time (minutes)	Weight change $\Delta g$ (mg)					
	support material					
	filter paper			brass gauze		
	original weight of sample (mg)					
	51.25	30.35	20.50	10.55	34.40	34.25
5	3.05	3.05	3.05	3.05	3.00	2.95
10	3.00	3.15	2.95	2.85	3.15	3.10
15	3.10	3.10	3.05	2.60	3.10	3.05
20	3.10	3.15	2.95	1.85	3.15	3.10
25	3.10	3.10	2.80	0.20	2.95	3.00
30	2.95	2.95	—	—	2.90	2.90
35	2.95	2.85	—	—	2.85	2.85
40	2.95	2.80	—	—	2.80	2.85
45	3.00	2.40	—	—	2.45	2.35
50	2.85	2.25	—	—	2.20	2.00
55	2.85	1.15	—	—	1.75	1.55
60	2.80	0.40	—	—	—	—

Therefore, on the basis of the above results, we used nitrogen at an average velocity of 1.38 cm/second (1.02 liter/minute) in order to eliminate uncertainties in the experimental conditions (temperature variations, and air convection currents in the cell). This is the minimum rate at which the temperature in the cell becomes uniform. At higher rates the pointer begins to vibrate.

To determine the influence of the nature of the supporting material on the kinetics of oil evaporation, the evaporability of OI oil and amynaphthalene from filter paper, tissue paper, and brass gauze was studied. The individual compound chosen was amynaphthalene, because its evaporation rate is constant and its boiling point is close to that of OI oil. It was found that uniform layers of oil or amynaphthalene on tissue paper can be obtained with samples not greater than 15 mg, and on filter paper, with samples not greater than 60 mg. Brass gauze is intermediate between the two. With larger samples, a ridge is formed along the lower edge of the strip or gauze. This ridge has no influence in the evaporation of amynaphthalene, but in the evaporation of OI oil it results in low values for the evaporation rate, and is therefore inadmissible.

Table 3 contains data on the evaporability of amynaphthalene from filter paper and brass gauze at 90°, with a current of nitrogen at 1.38 cm/second. It is seen that the evaporation rate of amynaphthalene is independent of the support material until about 40-50% of the original sample has evaporated, and then the rate decreases. The same is found with tissue paper.

The data in Table 3 also show that reproducible results are obtained by the proposed method for determination of oil evaporability. It is seen that in general the deviations are in the range of  $\pm 0.05$  mg, reaching  $\pm 0.1$  mg in some instances. This applies to a pointer sensitive to 0.05 mg. The limits are narrower with more sensitive pointers.

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# HYDROCARBONS OF THE DIPHENYLMETHANE SERIES AS HIGH-TEMPERATURE HEAT-TRANSFER MEDIA, AND THEIR PHYSICOCHEMICAL PROPERTIES

I. G. Matveev, N. I. Gel'perin, K. V. Vil'shau, and R. L. Globus

It is known that in a number of processes in the chemical, petroleum, food, and other industries, operating temperatures of 350° and over have to be maintained by supply or removal of heat. In such cases saturated steam or boiling water is unsuitable because of the high pressures involved (168 atmos at 350°). Therefore, heat engineering has long been faced with the search for available high-temperature heat-transfer media of low vapor pressures, low solidification points, good heat resistance, inertness towards ferrous metals, freedom from fire and explosion risks, with low viscosities in the liquid phase, and a high heat-transfer coefficient.

Numerous substances from various classes of organic and inorganic compounds have been suggested as heat-transfer media during recent years. These include a eutectic mixture of diphenyl with diphenyl oxide [1], fused salts [2], some organosilicon compounds [3-12], various aryloxy (polychloro or fluoro) alkanes and alkenes [13-15], ethers of polyhydric alcohols [16], glycerol [17], tetrachlorodiphenyl [18] alkylene glycols [19] polyalkylene glycol oils [20], the hydrocarbon fraction of petroleum recirculation gas [21], o-dichlorobenzene [22, 23], and fluorinated tertiary amines [24].

None of the compounds suggested so far is universal in satisfying all the requirements stipulated for heat-transfer media.

Investigations of the physicochemical properties of hydrocarbons of the diphenylmethane series have shown that they may be among the most suitable industrial high-temperature heat-transfer media [25].

Hydrocarbons of the diphenylmethane series (ditolylmethane, dicumylmethane, dixylylmethane, tetraisopropyldiphenylmethane, etc.) were prepared by condensation of aromatic hydrocarbons (toluene and higher homologs of benzene) with formaldehyde in presence of sulfuric acid



in the form of isomer mixtures, the composition of which was constant because of the method of synthesis. The Raman spectra of four samples of ditolylmethane, made in four different plants from different batches of raw material, were found to be the same.

It may be noted that individual data on the specific gravity, boiling points, and freezing points of some ditolylmethane isomers are available in the literature. The other hydrocarbons used in this work were synthesized for the first time by Matveev and Drapkina, and no data on their physicochemical properties are to be found in the literature.

We studied, in relation to their possible use as industrial heat-transfer media, the physicochemical properties of four members of the diphenylmethane series; their names, formulas, molecular weights, and conventional symbols are given below.

Hydrocarbons	Chemical formula	Molecular weight	Conventional symbol
Ditolylmethane	$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{CH}_3$	196	DTM
Dixylylmethane	$(\text{CH}_3)_2\text{C}_6\text{H}_3\text{CH}_2\text{C}_6\text{H}_3(\text{CH}_3)_2$	224	DXM
Dicumylmethane	$(\text{CH}_3)_2\text{HCC}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)_2$	252	DCM
Tetraisopropyldiphenylmethane	$[(\text{CH}_3)_2\text{HC}]_2\text{C}_6\text{H}_3\text{CH}_2\text{C}_6\text{H}_3[\text{CH}(\text{CH}_3)_2]_2$	336	TDM

The densities of these hydrocarbons were determined pycnometrically at a number of temperatures. The results ( $d_4$  g/cc) are given in Table 1.

It follows from Table 1 that the densities of DTM, DXM, DCM, and TDM are linear functions of the temperature.

Experimental data for DTM show that the heat capacities of these hydrocarbons can be determined to within 0.001 cal/kg · deg by means of V. Ia. Kurbatov's formula:

$$C = \frac{a + 0.1337t}{M} \quad \text{kcal/kg} \cdot ^\circ\text{C} \quad (1)$$

where M is the molecular weight of the hydrocarbon, and the values of a are given below.

Values of a in Formula (1)

Hydrocarbons:	DTM	DXM	DCM	TDM
a:	70.05	76.85	83.65	104.05

The hydrocarbon viscosities were determined by means of the Ostwald viscosimeter in the 20-150° range. The viscosities found are given in Table 2.

TABLE 1

Densities of DTM, DXM, DCM, and TDM at Various Temperatures

Temperature (°C)	DTM	DXM	DCM	TDM	Temperature (°C)	DTM	DXM	DCM	TDM
5.8	—	0.9899	—	—	65	0.9490	—	0.9190	—
7.0	—	—	—	(0.9408)	75	0.9420	—	—	—
20	0.9825	0.9797	0.9475	0.9278	75.7	—	(0.9849)	—	—
32.7	—	—	—	0.9192	80	0.9382	—	—	0.8872
34	—	0.9700	—	—	95	0.9274	—	0.8993	—
35	0.9710	—	—	—	120	0.9098	—	—	—
44.6	0.9636	—	—	—	135	—	—	0.8725	—
46	—	—	—	0.9099	150	0.8878	—	—	—
50	0.9600	—	0.9288	—	166	0.8786	—	—	—
60	—	—	—	0.9003	170	—	—	0.8427	—
63	—	0.9485	—	—	201	0.8478	—	—	—

At 150° the viscosities of all the hydrocarbons tend to become equalized, and approach the viscosity of water. This is very important, because viscosity is known to have a strong influence on the heat-transfer coefficient of liquid heat-transfer media.

The vapor pressures of DTM, DXM, DCM, and TDM were determined in the 50-160° range in a high-vacuum apparatus, by the method of vapor efflux from small orifices [26]. The results are given in Table 3.

The boiling points of DTM, DXM, DCM, and TDM at pressures  $P \geq 1$  atm, measured in metallic tubes fitted with manometers, are given in Table 4.

TABLE 2

Hydrocarbon Viscosities (in centipoises)

Temperature (°C)	Viscosities at temperatures (°C)								
	20	35	50	65	80	95	110	130	150
DTM	5.27	3.66	2.59	1.90	1.888	1.017	—	—	0.686
DXM	29.2	12.12	6.08	3.92	2.58	1.96	—	—	—
DCM	6.89	4.05	2.65	1.9	1.33	0.98	—	—	0.582
TDM	253	—	—	13.2	7.05	1.707	1.065	0.79	0.578

The data in Table 4 show that one advantage of these hydrocarbons is the higher boiling points under atmospheric pressure, as compared with such a common heat-transfer medium as a eutectic mixture of diphenyl and diphenyl oxide (258°).

The temperature-vapor pressure relationship for DTM, DXM, DCM, and TDM is represented very accurately by the following general equation:

$$\log P = A - \frac{B}{T}$$

where P is the pressure (mm Hg); T is the absolute temperature; A and B are coefficients the values of which are given below.

Coefficients	DTM	DXM	DCM	TDM
A:	8.61	11.20	9.09	8.77
B:	3290	5000	3850	3880

Another great advantage of these diphenylmethane hydrocarbons is the wide temperature range in which they exist in the liquid state. In contrast to the eutectic mixture of diphenyl and diphenyl oxide, which solidi-

TABLE 3

Vapor Pressures of DTM, DXM, DCM, and TDM at Various Temperatures

Temperature (°C)	Vapor pressure (mm Hg)			
	DTM	DXM	DCM	TDM
30	0.00581	—	—	—
50	0.017	—	0.00275	—
71	—	—	—	0.00295
86.7	—	—	—	0.00871
90	0.2687	—	0.0409	—
108.5	0.982	—	0.085	—
110.7	—	0.0167	—	—
125	—	—	—	0.0852
128.5	2.49	—	0.418	—
136.7	—	0.0896	—	—
143.4	—	—	—	0.2545
160	—	0.2499	—	0.591

TABLE 4

Boiling Points of DTM, DXM, DCM, and TDM at P ≥ 1 atm

Pressure P (atm)	Boiling point (°C)			
	DTM	DXM	DCM	TDM
1.0	292	324	335	384
1.5	314	—	360	—
2.0	332	364	374	394.5
2.5	345	372	388	—
3.0	354	382	398	408
3.5	363	391	408	—
4.0	372	400	418	420
4.5	380	407	426	—
5.0	388	412	431	427

flies at 12.3°, DTM, DXM, DCM, and TDM solidify at much lower temperatures. In this respect they are superior to all the high-temperature organic heat-transfer media suggested up to now, with the exception of organo-silicon compounds. The solidification temperatures ( $t_s$ ), flash points ( $t_f$ ), and surface tensions ( $\sigma$ ) of the hydrocarbons are given below.

Properties	DTM	DXM	DCM	TDM
$t_s$ (°C)	-32 to -36	-40 to -44	-22 to -44	-8
$t_f$ (°C)	142 to 146	161	160	182
$\sigma$ at 21° (dynes/cm)	38.2	—	34.4	—

The thermal conductivities of DTM, DCM, and TDM were determined by means of a spherical double calorimeter under steady-state conditions in the temperature range from -10 to +98°.

The following values were obtained for the thermal conductivities (kcal / m · hour · deg):

$t$ (°C)	-10.25	+2	23.5	25.9	48.2	65.1	67.4	91.7	96.2
$\lambda_{DTM}$	0.1220	0.113	0.1155	0.1180	0.1075	0.1060	0.1040	0.1025	0.0987
$t$ (°C)	-8	+15	20.5	29	40	51	69	98	—
$\lambda_{DCM}$	0.1125	0.1100	0.1045	0.0980	0.0975	0.094	0.0885	0.0765	—
$t$ (°C)	20	44	75.5	—	—	—	—	—	—
$\lambda_{TDM}$	0.0945	0.0905	0.082	—	—	—	—	—	—

It is seen that the thermal conductivity falls with increasing temperature and molecular weight.

Ditolylmethane was found to have the best heat resistance in plant and laboratory tests. The laboratory tests were performed in metallic tubes fitted with reflux condensers, with the ditolylmethane boiling continuously and the condensed vapor returning to the tubes. The results of the tests are given in Table 5.

TABLE 5

Changes in the Properties of Ditolylmethane During Prolonged Boiling at Atmospheric Pressure in Laboratory Conditions

Properties	Boiling time, months			
	1	2	3	4
Density at 20° (g/cc)	0.9952	1.0011	0.9964	1.0001
Viscosity at 20° (centipoises)	9.17	8.9	7.2	7.5
Start of Boiling (°C)	287	290	291	283
80% distills at (°C)	307	312.5	—	360
90% distills at (°C)	310	333	322	—
Flash point (°C)	146	145	143	144

It must be noted that after 90% of the ditolylmethane had been distilled off, and the corresponding temperature indicated in Table 5 had been reached, the residue crystallized.

When ditolylmethane was used as a heating medium for plant equipment, the results given below were obtained.

The heat resistance of DCM and TDM was determined under laboratory conditions only, during continuous boiling (as for DTM). The result are given in Table 6.

The residue after distillation of 90% of dicumylmethane which had been boiled for three months began to decompose above 360°.

The residue after distillation of 90% of tetraisopropyldiphenylmethane which had been boiled for one month began to decompose at ~402°.

Laboratory tests showed that boiling liquid DTM and DCM, and their condensing vapors, have no effect at all on carbon steel.



# Heat Resistance of Ditolylmethane under Plant Conditions

Service time	Density at 20° (g/cc)	Viscosity at 20° (centipoises)	Start of boiling (°C)	90%DTM distills at (°C)
2 months of use at 260° . .	0.9862	5.24	281	293
4 months of use at 260° . .	0.9865	5.50	288	292
4076 hours of use at 290—				
300° . . .	0.9896	7.00	—	—
5276 hours of use at 290—				
300° . . .	0.9855	6.70	287.5	310

TABLE 6

Changes in the Properties of DCM and TDM During Continuous Boiling at Atmospheric Pressure in Laboratory Conditions.

Properties	Boiling time (months)				
	DCM				TDM
	1	2	3	4	1
Density at 20° (g/cc)	0.9918	1.0055	1.0074	0.9622	1.1078
Viscosity at 20° (centipoises)	10.8	9.6	12.2	11.8	76.0
Start of boiling (°C)	294	—	—	—	361
80% distills at (°C)	343	344	348	351.5	397
90% distills at (°C)	346	344.5	360	365	—
Flash point (°)	158	157	146	146.5	140

## SUMMARY

1. Hydrocarbons of the diphenylmethane series satisfy all the requirements of industrial high-temperature heat-transfer media. They have high boiling points at atmospheric pressure, relatively low vapor pressures at high temperatures, low freezing points, good heat resistance, are nontoxic, and are noncorrosive to carbon steel.
2. Hydrocarbons of the diphenylmethane series can be used as heat-transfer media either in the liquid or in the vapor state.
3. The highest heat resistance is found in ditolylmethane, and the lowest in tetraisopropyldiphenylmethane; the latter showed an appreciable density increase and a considerable lowering of the flash point when boiled for one month at atmospheric pressure.
4. The hydrocarbons of the diphenylmethane series are almost identical in heat capacity, the heat capacity—temperature relationship, and thermal conductivity, with the eutectic mixture of diphenyl and diphenyl oxide, which is the commonest heat-transfer medium. However, this mixture is considerably inferior to the hydrocarbons in all other physical properties, including heat resistance.

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# EFFECT OF THE AMOUNT OF CATALYST ON INTENSIFICATION OF THE DESTRUCTIVE HYDROGENATION OF PETROLEUM RESIDUES IN THE LIQUID PHASE

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It is known from the literature that individual unsaturated and sulfur-containing compounds are hydrogenated fairly completely under conditions of destructive hydrogenation at moderate pressures, about 20-50 atm, in presence of high-temperature hydrogenation catalysts [1-6].

Exhaustive hydrogenation of individual aromatic compounds cannot be effected in autoclaves at high temperatures and pressures, about 200 atm, although under these conditions the thermodynamic equilibrium is shifted completely in the direction of hydride formation. The degree of hydrogenation is considerably greater in continuous systems at 200 atm at low space velocities ( $1.1 \text{ liter}^{-1} \cdot \text{hour}^{-1}$ ) [7-13].

The degree of hydrogenation reached for individual compounds cannot be achieved in liquid-phase destructive hydrogenation of petroleum residues under high pressures. The hydrogenation products always contain unsaturated and sulfur compounds, as well as aromatics, and also condensation products [14-15]. The reason is that the catalyst, generally used in small quantities (1-2 wt. % in destructive hydrogenation with a suspended catalyst, and up to 20% in autoclave experiments), was rapidly deactivated by the asphaltic and tarry components of the raw material.

It has been reported [14, 16] that the degree of hydrogenation increases with increasing catalyst concentration in the raw material. However, the degree of hydrogenation attained was still inadequate (as shown by the higher densities of the residues as compared with the original raw material), because the variations of the catalyst charge were confined to relatively narrow limits (from 0 to 20%).

The purpose of this investigation was to study the possible intensification of liquid-phase destructive hydrogenation by means of a considerable increase of the catalyst concentration in the raw material.

## EXPERIMENTAL

The raw materials used in the experiments were mazut (black oil) and semiasphalt from Tuimazy (Devonian) oil; the characteristics are given below:

$d_4^{20}$	Content of fraction up to 400° (wt. %)	Asphaltene content (wt. %)	Sulfur content (wt. %)
Mazut . . . . . 0.962	15.0	8.8	2.0
Semiasphalt . . . 1.005	0.0	15.6	3.0

The industrial catalysts used were tungsten sulfide ( $\text{WS}_2$ ) and molybdenum oxide (14%  $\text{MoO}_3$  on  $\text{Al}_2\text{O}_3$ ).

Experimental procedure. The experiments were performed in a rotary autoclave of 0.9 liter capacity. A mixture of the finely divided catalyst and the preheated raw material (at 70°) was put into the autoclave,

hydrogen was pumped in to the required pressure, and the electric heater was switched on. The temperature was regulated by means of a rheostat.

At the end of the experiment the autoclave was cooled and emptied. As in most of the experiments a large amount of catalyst was used, and most of the product was adsorbed on it, the product was not decanted separately, and the total weight of the mixture was used in the balance calculations. The mixture was put into a Claisen flask, and the gasoline and part of the kerosene fractions were distilled off on a glycerol bath, first under atmospheric pressure and then under vacuum. The residue was extracted with chloroform in a Soxhlet apparatus, the solvent was evaporated off, and the residue was fractionated under vacuum.

The material balance was calculated from the fractionation data and analytical data for the coke on the catalyst.

For determination of the amount of coke on the catalyst, a weighed sample of the catalyst was placed in a quartz loop and calcined at 600° in a current of air. The gas was passed through potassium permanganate solution to absorb SO<sub>2</sub>, and then analyzed in the All-Union Heat Engineering Institute apparatus. The amount of coke on the catalyst was calculated from the contents of CO and CO<sub>2</sub> in the gas.

The hydrogen consumption was found from the gas-analysis data.

## DISCUSSION AND RESULTS

Effect of the amount of catalyst. Data on the effect of the amount of catalyst (tungsten sulfide) on the yield and quality of the hydrogenation products are given in Table 1 and Figs. 1 and 2; it is seen that as the catalyst charge increases, the total yield of liquid products decreases slightly; the amount of added hydrogen increases, so that the yield of light fractions is greater and the amount of residue is less; the iodine number of the gasoline fraction falls to zero, and the density of the residue falls to 0.88 with 200 wt. % on WS<sub>2</sub>.

It follows from Table 1 that the coke yield calculated on the raw material is directly proportional to the amount of catalyst used in the experiment, whereas the amount of coke on the catalyst depends little on the amount of the latter.

This is the reason for the decreased yields of liquid products with increase of the amount of tungsten sulfide.

This cannot be the sole explanation for the decreased yields of residue with increase of the catalyst charge, as the yield of the residue diminishes more rapidly than the total yield of liquid products; increase of the degree of hydrogenation influences the decrease of the residue yield. Thus, despite the rapid increase of the hydrogenation rate with increasing amounts of catalyst, the yield of coke calculated on the raw material must be taken into consideration in selection of the optimum conditions.

It follows from Table 1 that the best conditions with regard to the material balance and the quality of the products are those of Experiment 42 (100% WS<sub>2</sub>). Under these conditions, Devonian oil semiasphalt yields 82% of liquid products on the raw material; the fractions up to 200°, and 200-360°, contain no unsaturated compounds, are almost sulfur-free, while the residue above 400° has density 0.92; the coke yield on the raw material is 5 wt. %.

### Chemical Composition of Fraction Boiling up to 200°

Unsaturated	Aromatics	Paraffins	Naphthenes
0.5	23.7	35.7	39.8

### Chemical Composition of 200-325° Fraction

Unsaturated	Aromatics	Paraffins	Naphthenes
1.9%	42.6%	25.4%	30.0%

Nine experiments were performed under the conditions of Experiment 42, in order to determine the chemical group composition of the products.

TABLE 1

Effect of Amount of Catalyst on the Liquid-Phase Destructive Hydrogenation of Semiasphalt.  
Hydrogenation Time 10 Minutes

Experimental conditions	Experiments No						
	52	58	53	54	60	42	43
Amount of catalyst (wt. %)	9	25	46	70	47	100	200
Average temperature (°C)	442	455	448	445	445	452	450
Hydrogen pressure (atm):							
initial	140	130	140	140	142	145	140
maximum	230	300	220	295	310	300	280
Molar ratio of H <sub>2</sub> to raw material	88 : 1	88 : 1	82 : 1	82 : 1	82 : 1	82 : 1	81 : 1
Amount of H <sub>2</sub> combined (wt. % on raw material)	2.2	2.2	2.3	3.0	3.0	3.7	5.8
Amount of coke on catalyst (wt. %)	7.2	7.0	8.6	6.8	6.8	5.0	4.8
Material balance (wt. %):							
gas and losses	13.7	12.7	7.4	12.3	9.0	12.9	14.9
gasoline to 200°	—	1.8	7.7	8.5	9.4	10.5	13.5
200-360° fraction	1.6	5.8	4.0	4.5	9.6	17.6	22.0
360-400° fraction	5.5	4.4	4.4	2.9	6.8	12.0	6.0
residue above 400°	79.5	73.6	72.5	67.5	60.0	42.0	34.0
total liquid products	85.6	85.6	88.6	83.4	85.8	82.1	75.5
coke	0.7	1.7	4.0	4.8	5.2	5.0	9.6
Quality of fraction up to 200°:							
iodine number	—	81	25	6.0	0.5	0	0
sulfur (wt. %)	—	0.31	0.26	0.15	—	0.06	0.04
sulfonables (vol. %)	—	83	—	29	26	23	24
Quality of 200-360° fraction:							
iodine number	22	24	24	5	6	0	0
sulfur (wt. %)	—	0.85	0.42	0.35	—	0.11	0.07
sulfonables (vol. %)	60	46	46	45	45	42	37
Quality of 360-400°:							
iodine number	10	22	10	10	10	5	0
sulfonables (vol. %)	68	53	19	49	54	51	37
Quality of residue above 400°:							
density d <sub>4</sub> <sup>20</sup>	1.023	0.998	0.997	0.989	0.978	0.920	0.876
asphaltenes (wt. %)	21.0	—	15.8	11.6	7.3	0.45	0.35

**Role of the initial hydrogen pressure.** After it had been shown that destructive hydrogenation in the liquid phase can be considerably intensified by the use of large amounts of tungsten sulfide, it was desired to determine the role of the initial hydrogen pressure. The results of experiments with different initial hydrogen pressures (200% of tungsten sulfide was used) are plotted in Figs. 3 and 4. In comparison of the experimental results for different initial pressures it must be remembered that in this case (in contrast to continuous systems) two factors alter simultaneously; the total pressure, and the partial pressure of hydrogen.

It follows from Figs. 3 and 4 that, as was to be expected, decrease of the initial pressure to 1/3 has little effect on the yields of the products. With regard to the quality of the products, the following is found; the quality of the fraction up to 200° is almost independent of the initial hydrogen pressure, the quality of the residue varies very appreciably with the pressure, and the other fractions occupy an intermediate position. The coke yield on the raw material depends very little on the initial pressure, and is determined by the amount of WS<sub>2</sub>.

**Effect of the duration of the experiment.** It is known that the duration of the experiments in autoclaves cannot be determined exactly. In the present instance, with experiments under hydrogen pressure in presence of catalysts, the corrections for heating and cooling times such as are applied in experiments on thermal cracking in autoclaves [17] are inapplicable. The experimental times as determined in the present investigation are nominal; while the method used did not give the absolute time, it gave an indication of the effect of relative changes in the times on the process.

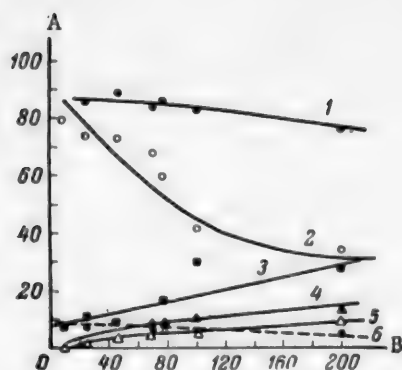


Fig. 1. Effect of the amount of  $WS_2$  on the yield of hydrogenation products. Temperature 445-455°, duration of experiments 10 minutes, initial hydrogen pressure 130-140 atm. A) Yield of products (wt. % on raw material), B) amount of  $WS_2$  (wt. %). Yields: 1) total liquid products, 2) residue above 400°, 3) 200-400° fraction, 4) gasoline fraction, 5) coke, 6) coke on catalyst (wt. %).

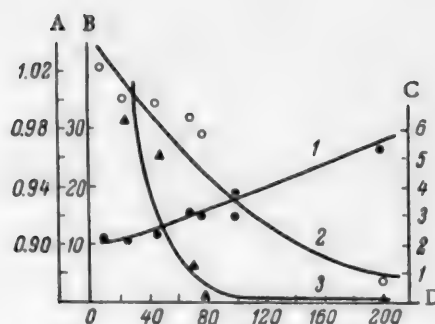


Fig. 2. Effect of the amount of  $WS_2$  on the degree of hydrogenation. Temperature 445-455°, duration of experiments 10 minutes, initial hydrogen pressure 130-140 atm. A) Density  $d_4^{20}$ , B) iodine number, C) amount of hydrogen combined (wt. %), D) amount of  $WS_2$  (wt. %). Curves: 1) amount of hydrogen combined, 2)  $d_4^{20}$  of residue above 400°, 3) iodine number of gasoline fraction.

The start of the experiment was taken to be the instant at which the temperature in the autoclave reached 445°. The heating time from 300° (this is the temperature at which appreciable thermal cracking of the heavy products begins) to 445° was usually about 20 minutes. The following experiment was performed to determine

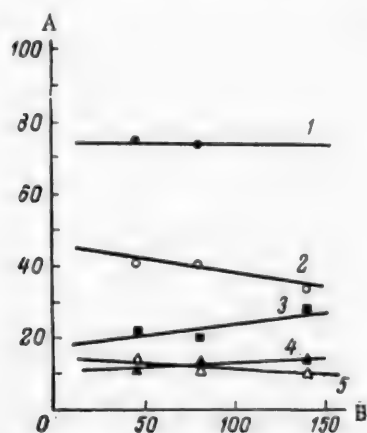


Fig. 3. Effect of pressure on the yields of hydrogenation products. Temperature 450°, duration of experiments 10 minutes, amount of  $WS_2$  200%. A) Yield of products (wt. % on raw material), B) initial hydrogen pressure (atm). Yields: 1) total liquid products, 2) residue above 400°, 3) 200-400° fraction, 4) gasoline fraction, 5) coke.

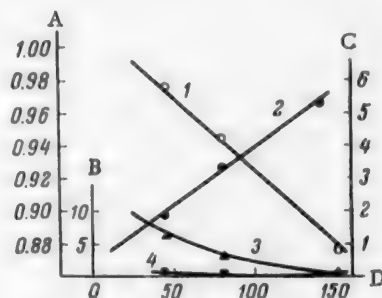


Fig. 4. Effect of pressure on degree of hydrogenation. Temperature 450°, duration of experiments 10 minutes, amount of  $WS_2$  200%. A) Density  $d_4^{20}$ , B) iodine number, C) amount of hydrogen combined (wt. %), D) initial hydrogen pressure (atm.). Curves: 1)  $d_4^{20}$  of residue, 2) amount of hydrogen combined, 3) iodine number of 360-400° fraction, 4) iodine number of gasoline fraction.

the degree of conversion of the mazut at the zero time: the autoclave temperature was raised to 445° in the usual way, and the heating and rotation of the autoclave were then stopped. The duration of this experiment was taken nominally as zero. Table 2 contains data on the yields and quality of the products in experiments of different duration, in presence of 25 and 100% of tungsten sulfide. It is seen that the duration of the experiment has different effects on the product composition and quality, according to the amount of catalyst used.



In presence of 100 wt. %  $WS_2$ , cracking and hydrogenation have already proceeded to a considerable extent by the start of the experiment. Further heating at the experimental temperature does not alter the total yield of liquid products, changes their fractional composition only slightly, and has a very appreciable influence on the quality of the products formed: the iodine number of the fraction up to 200° decreases, coke formation is reduced, and the density (and the yield) of the residue decrease.

TABLE 2

Effect of Duration of the Experiment on the Destructive Hydrogenation of Semiasphalt (Temperature 445-455°)

Experimental conditions	Experiment No.				
	56	48	42	58	49
Nominal duration (minutes)	0	5	10	10	60
Hydrogen pressure (atm):					
initial	140	138	145	130	148
maximum	290	290	300	300	330
Molar ratio of $H_2$ to raw material	32 : 1	32 : 1	32 : 1	38 : 1	35 : 1
Amount of catalyst (wt. %)	96	100	100	25	26
Amount of $H_2$ combined (wt. % on raw material)	3.0	3.4	3.7	2.2	3.8
Amount of coke on catalyst				7.0	7.0
Material balance (wt. %):					
gas and losses	8.0	6.2	5.0		
fraction to 200°	8.1	16.1	12.9	12.7	17.7
200-360° fraction	7.2	8.1	10.5	1.8	12.2
360-400° fraction	7.5	9.4	17.6	5.8	11.6
residue above 400°	7.0	6.2	12.0	4.4	6.7
total liquid products	62.5	54.0	42.0	73.6	50.0
coke	84.2	77.7	82.1	85.6	80.5
Quality of fraction up to 200°:					
iodine number	7.7	6.2	5.0	1.7	1.8
sulfur (wt. %)	4	3	0	31	19
sulfonables (vol. %)	0.1	0.04	0.06	0.31	0.17
Quality of 200-360° fraction:					
iodine number	26	19	23	33	22
sulfur (wt. %)	7	4	0	24	12
sulfonables (vol. %)	0.54	0.18	0.11	0.85	0.31
Quality of 360-400° fraction:					
iodine number	48	42	42	46	39
sulfonables (vol. %)	15	5	5	22	12
Quality of residue above 400°:					
density $d_4^{20}$	54	50	51	53	43
asphaltenes (wt. %)	0.977	0.944	0.920	0.998	0.990
	3.7	1.7	0.45	—	12.5

Quite different results are obtained with 25 wt. %  $WS_2$ . Here the fractional composition of the products changes considerably with increase of the time, while changes in their quality are slight; i.e., in this case the role of the catalytic processes decreases and thermal cracking becomes significant.

It follows that in liquid-phase hydrogenation of heavy petroleum residues hydrogenation processes develop extensively only in presence of large amounts of catalyst. Otherwise the whole character of the process is determined by thermal cracking, and hydrogenation reactions result only in retardation of coke formation and some decrease of the amount of unsaturated compounds.

Effect of the nature of the raw material. Comparative experiments (with 100%  $WS_2$ ) showed that there are no significant differences between the autoclave hydration of mazut and semiasphalt at initial hydrogen pressure of 140 atm.

If the initial pressure is 40-45 atm, the products formed by the hydrogenation of semiasphalt have higher sulfur and asphaltene contents (0.36% sulfur in the 200-360° fraction, 4.3% asphaltenes in the residue above 400°).

Hydrogenation experiments with the tungsten catalyst showed that the amount of coke deposited on the catalyst is very considerable, and varies little with the experimental conditions.

Despite the high catalytic activity of tungsten sulfide, it cannot be used in a continuous process for destructive hydrogenation of heavy petroleum products, as when the coke deposits are burned out the active tungsten sulfide is converted into the much less active tungsten oxide. The oxide can be converted back into the sulfide only by chemical methods. It is thus impossible in practice to regenerate the tungsten sulfide. A sufficiently active oxide catalyst therefore had to be found.

Several oxide catalysts were tested in the autoclave by the method described above. The best results were obtained with alumina-molybdenum oxide catalyst No. 7360 (14% MoO<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub>). As is seen from the data below, 84% of liquid products was obtained from Tuimazy semiasphalt at 460°, initial hydrogen pressure 150 atm (maximum pressure 340 atm), in experiments lasting 10 minutes, with 100% of catalyst.

#### Material Balance

(in wt. % on the raw material)

Fraction up to 230°	13.0
230-360° fraction	23.0
Residue above 360°	48.0
Liquid products	84.0
Coke	5.1
Gas + losses	10.9
Total	100.0

Data on the quality of the products are presented below:

	Iodine number	Sulfon- ables (vol. %)	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	Sulfur (wt. %)	Asphalt- enes (wt. %)
Fraction up to 230°	0.5	33.4	1.4590	0.8216	0.05	—
230-360° fraction	2.5	47.3	1.5068	0.9056	0.55	—
Residue	—	—	—	—	—	2.4

#### SUMMARY

1. The liquid-phase destructive hydrogenation of semiasphalt from Tuimazy (Devonian) petroleum was studied in an autoclave over tungsten sulfide, with the catalyst charge varied from 10 to 200 wt. %; it was found that liquid-phase destructive hydrogenation can be intensified considerably by increase of the catalyst concentration in the raw material, in the conversion of heavy-petroleum residues. The optimum catalyst content is 100% on the weight of the raw material.

2. The hydrogenation of mazut and semiasphalt is accompanied by considerable deposition of coke on the catalyst, irrespective of the working pressure, which was varied in the range of 330 to 110 atm in the experiments, and of the amount of catalyst used.

3. The amount of coke deposited on the catalyst in the hydrogenation of these materials varied in the range of 4.8-8.0% by weight.

4. The yield of coke, calculated on the raw material, is directly proportional to the weight ratio of catalyst to raw material.

5. Continuous hydrogenation without regeneration of the catalyst by combustion of the coke deposits is impossible. Sulfide catalysts are therefore unsuitable, and easily-regenerated oxide catalysts must be used.

6. Good-quality liquid products are obtained in high yields with the use of an alumina-molybdenum oxide catalyst.

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## KINETICS OF THE OXIDATIVE CONVERSION OF HYDROCARBONS IN THE LIQUID PHASE\*

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Investigation of the kinetics of the reaction stages in the liquid-phase oxidation of higher paraffins is very difficult because of the great diversity of the reaction products; little work has been done on their separation. The collection of the volatile oxygen-containing substances carried away in the exit stream of the oxidizing gas also involves considerable difficulties.

A usual method for the experimental determination of kinetic data on such reactions is the study of changes in the contents of functional groups, such as peroxide, hydroxyl, carbonyl, etc., in the course of oxidation. This method gives some measure of a true indication of the yields and the course of the process. However, this method has been subjected to valid criticisms [1, 2], and because of the inadequate accuracy and difficulty in interpretation of the results, it must be regarded as suitable mainly for studies of the initial oxidation stages [1]. It is especially inaccurate when applied to estimations of reaction rates in the oxidative breakdown of a hydrocarbon molecule with the formation of two or more oxygen-containing derivatives, and also in the presence of bifunctional and multifunctional compounds.

A method fairly often used is based on measurements of the amount of oxygen absorbed in the course of a reaction. However, the data so obtained are inadequate if considerable amounts of substances differing in their oxygen contents are formed [3].

In our opinion, a method for determination of the amount of the original substance reacting per unit time is a necessary supplement to the existing methods. The most suitable procedure for this purpose was found to be by adsorption chromatography on silica gel, used by E. M. Nebylova in our laboratory for analysis of the oxidation products.

The purpose of the present investigation was to obtain direct data on the rates and kinetics of hydrocarbon conversion under conditions similar to those used in batch oxidation for the production of higher fatty acids.

The experiments were performed in Tsykovskii's oxidation column [1], 45 mm in diameter. The air rate, constant in all the experiments at 8 liters/minute, corresponded to the transition to a kinetic mechanism of oxygen absorption. The initial hydrocarbon charge was 300 g. The design of the column condenser and the circulation of water through it were such that the hydrocarbons entrained in the exit gas were returned to the reaction zone.

The oxidation of individual hydrocarbons, and of a technical mixture – a synthine Diesel fraction (b.p. 220–330°) – was studied. The individual hydrocarbons were prepared by A. I. Levin in our Institute, in the form of one-degree fractions obtained by sharp fractionation of synthine. These fractions were treated with

\* Communication II in the series "Certain characteristics of liquid-phase oxidation of hydrocarbons, initiated by metal salts."

100%  $H_2SO_4$  and caustic soda solution, washed with water, and dried. Analytical data for the n-tridecane and n-tetradecane used are given in Table 1.

TABLE 1

Analytical Data for Hydrocarbons

Hydrocarbon	Boiling point (°C)	Molecular wt.	Elementary composition (°C)		Empirical formula	Refractive index $n_D^{20}$	Isomer content (%)
			C	H			
n-Tridecane	283.5—294.5	180.6	84.6	15.4	$C_{12.6}H_{27.5}$	1.4255	13.9
n-Tetradecane	252—252.5	197.8	85.3	14.7	$C_{14.0}H_{30.0}$	1.4288	9.2

It follows from Table 1 that the hydrocarbons contained an admixture of isomers, determined by extractive crystallization with carbamide [4]. The molecular weight was determined cryoscopically in benzene.

The contents of unchanged hydrocarbon were determined in samples taken during the reaction. O'Connor's method [5], as modified by Guliaeva and Pyshkina [6], was used. The method is based on the adsorption of oxygen compounds from the sample on anhydrous silica gel, in presence of an azo dye, soluble in hydrocarbons, which is adsorbed much more strongly than hydrocarbons of any structure. Therefore the appearance of a colored filtrate in the course of elution indicates the transition from a hydrocarbon fraction to a fraction containing oxygen compounds. The silica gel was "chromatographic" grade, from the "Krasnyi Khimik" factory (activity 10-12 g of acetone per 100 g of adsorbent), the solvent was benzene, the eluant was methanol, and the dye was fat-soluble indigo red. The diameter of the adsorption column was 10 mm. The weight of the substance taken (1.5-3.0 g) and amount of silica gel (10-30 g) were calculated by the usual method, in accordance with the expected contents of the oxygen compounds and the adsorbent activity.

Adsorption-displacement chromatography on silica gel was first used for studies of n-tridecane conversion. The n-tridecane was oxidized in presence of 0.3% of Mn naphthenate (calculated as the metal) at 130°. The experimental results are presented in Table 2. For comparison of the degree of conversion with acid formation, the saponification and acid numbers are given.

It follows from Table 2 that soon after the reaction has developed, the rate of hydrocarbon conversion becomes constant, and shows no tendency to change up to ~50% conversion. This indicates the existence of a liquid-phase oxidation stage, which may be termed the stable stage, and which proceeds as a zero-order reaction at the rate  $w = -\frac{dx}{dt} = k$ . The average rate of the stable stage was found to be  $w = 0.10$  molar %/minute.

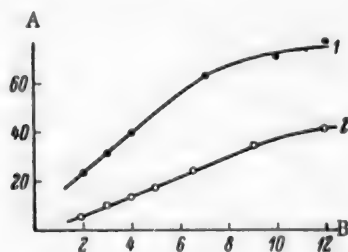


Fig. 1. Oxidation of synthine in presence of Mn naphthenate. A) Amount of hydrocarbon converted (%), B) yield of water-insoluble acids (in g/100 g of synthine). Curves: 1) hydrocarbon conversion, 2) yields of water-insoluble acids.

Similar results were obtained in the oxidation of a technical hydrocarbon mixture — synthine — under the same experimental conditions. It is clear from the experimental results plotted in Fig. 1 that the formation rate of the water-insoluble acid also remains constant for a considerable period. Subsequently, with decrease

of the hydrocarbon conversion rate, the formation of water-insoluble acids slows down. It is likely that here as in some other instances (for example, see the curve for the conversion of tetradecane at 155°, Fig. 3), there is a limit to the consumption of the original substance in liquid-phase oxidation.

TABLE 2

Experimental Data on the Oxidation of n-Tridecane

Time from start of oxidation (min)	Hydrocarbon content of sample (%)	Amount of hydrocarbon converted (%)	Conversion rate (molar %/minute)	Acid number (mg KOH per g)	Saponification number (mg KOH per g)
15	97.34	2.66	0.177	3.00	3.75
30	95.33	4.67	0.134	3.55	5.17
70	92.66	7.34	0.105	4.92	14.42
130	87.33	12.67	0.098	10.13	23.78
190	80.33	19.67	0.104	18.13	36.87
250	75.33	24.67	0.099	27.27	55.92
310	65.66	33.34	0.107	37.98	74.77
370	62.66	37.34	0.101	49.50	94.13
430	58.33	41.77	0.097	60.38	114.77
495	49.50	50.50	0.102	71.06	135.71

\* Times given without the induction period.

Bashkurov [7] used indirect analytical methods (determination of the functional-group content) to demonstrate that the rate of liquid-phase oxidation of paraffins to alcohols is independent of the degree of conversion. Our results are also in agreement with Leibnitz's data [2] concerning the constant rate of heat liberation in paraffin oxidation.

Several other oxidation chain reactions, which are best represented by the equation  $w = \text{constant}$  over considerable periods, were discussed by Semenov [8] as long ago as 1934.

By the modern theory, liquid-phase oxidation by molecular hydrogen is a chain reaction with degenerate branching [9]. The branching is caused by hydroperoxides which decompose according to the equation  $\text{ROOH} \rightarrow \text{RO} \cdot + \cdot \text{OH}$ , with the formation of active free radicals  $\text{RO} \cdot$ , which initiate new chains. As a rule,

self-acceleration of the oxidation reaction is the consequence of this process. In liquid-phase conditions, the absence of acceleration may be ascribed to the probable self-retardation of the reaction by its products which have an inhibiting effect, such as alcohols.

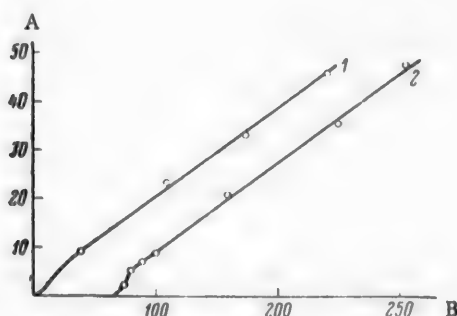


Fig. 2. Effect of addition of cetyl alcohol to the original tetradecane. A) Amount of hydrocarbon converted (molar %), B) time (hours). 1) Oxidation of tetradecane in presence of cetyl alcohol, 2) without cetyl alcohol.

curve, was unchanged by the preliminary addition of cetyl alcohol. The considerable shortening of the induction period in presence of the alcohol can be attributed to the accelerating action of alcohols on the

Knorre [10] has shown that the effect of weak inhibitors is most pronounced if they are introduced at the initial oxidation stage. We tested the possible inhibiting action of high-molecular alcohols in liquid-phase oxidation. This was done by comparative experiments on the oxidation of n-tetradecane in presence of 0.3 wt.% of Mn stearate, with and without the addition of 0.75 wt. % of cetyl alcohol before the start of oxidation. It follows from the results, plotted in Fig. 2, that the rate of hydrocarbon conversion, 0.177 molar %/minute, determined from the slope of the linear region of the kinetic



conversion of  $Mn^{2+}$  into a higher valence state with the formation of a multinucleate complex [11].\*

Further, as in the preceding experiments, there is no connection between the rate of the developed reaction and the duration of induction period preceding it.

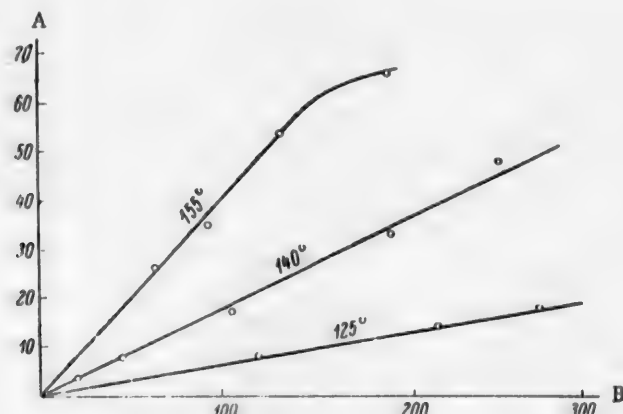


Fig. 3. Conversion of n-tetradecane by oxidation in presence of Mn stearate at various temperatures. A) Amount of hydrocarbon converted (molar %), B) time (in minutes, without the induction period).

The fact that the reaction rate is independent of the degree of hydrocarbon conversion greatly simplifies determination of the activation energy. Such a determination was performed for the oxidation of n-tetradecane. An important fact is that the molecular weight of this hydrocarbon is close to the average value for the mixtures of low-melting paraffins promising for industrial use [12].\*\* The oxidation was performed in presence of 0.3 molar % of Mn stearate. The end of the initial stage (induction period) was determined as described in the

TABLE 3

Experimental Data on the Oxidation of n-Tetradecane

Temperature (in °C)	Duration of induction period (minute)	Rate constant k for the conversion of the hydro- carbon in the stable stage ( $\text{min}^{-1} \cdot 10^2$ )
125	230	0.064
140	75	0.177
155	25	0.400
170	10	—

preceding paper [11]. The results of the experiments are presented in Table 3 and Fig. 3. A reliable value of the reaction rate at 170° was not obtained because of the loss of hydrocarbon from the reaction zone.

The determination of the activation energy for the initial reaction stage was based on the relationship between the logarithm of the reciprocal induction period  $\frac{1}{\tau}$  and  $\frac{1}{T}$ , and the fact that the rate constant of the

\* An important role may also be played by neutral acidic radicals formed by thermal decomposition of organic salts of manganese in higher valence states. Such decomposition is probable, by analogy with available data on lead tetraacetate (Fieser) and manganese triacetate (Zonis). A relatively weak acidic radical can react with an alcohol to give a strong alkoxy radical:  $\text{RCOO} \cdot + \text{HOR}' \longrightarrow \text{RCOOH} + \cdot \text{OR}'$ .

\*\*As in original - Publisher's note.

initial stage  $k \approx \frac{1}{\tau}$ .

The activation energies of the initial and stable stages of the reaction found from Fig. 4 and 5, 24 and 21 kcal/mole respectively, are close to the values usually found for oxidation chain reactions of saturated hydrocarbons. The higher value for the activation energy in the initial period is probably the consequence of the

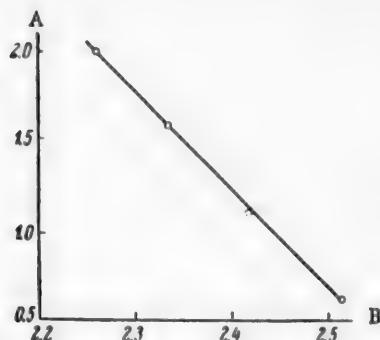


Fig. 4. Plot of the rate constant for the initial stage of tetradecane oxidation against  $\frac{1}{T}$ , for determination of the activation energy.  $E = 24$  kcal.

A)  $\log \frac{1}{\tau} \cdot 10^3$ , B)  $\frac{1}{T} \cdot 10^3$ .

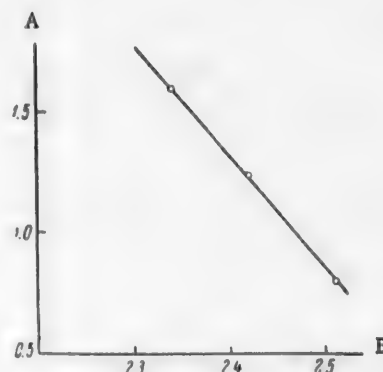


Fig. 5. Plot of the rate constant for the developed stage of tetradecane oxidation against  $\frac{1}{T}$ , for calculation of the activation energy.  $E = 21$  kcal.

A)  $\log k \cdot 10^3$ , B)  $\frac{1}{T} \cdot 10^3$ .

predominance of more difficulty activated elementary reaction during this stage. For example, the initiating reaction  $RH + O_2 \rightarrow RO_2 + \cdot HO_2$ , probably has an activation energy of  $\sim 50$  kcal/mole [10]. Elementary reactions involving  $Me^{2+} \rightarrow Me^{3+}$  transition may also be significant here.

The reaction order of hydrocarbon conversion during the induction period cannot be established as yet, because low concentrations of oxygen compounds cannot be determined with sufficient accuracy. From the data in Table 3, the following expression is obtained for the effect of temperature on the induction period in the oxidation of tetradecane in presence of  $Mn^{2+}$  stearate:

$$\frac{1}{\tau} = 1.1 \cdot 10^{10} e^{-\frac{24000}{RT}} \text{ sec}^{-1}.$$

For the stable stage of the reaction, a value of  $3.7 \cdot 10^6 \text{ second}^{-1}$  was found, from the reaction rates at various temperatures, for the preexponential term. Hence the reaction rate as a function of temperature can be presented by the equation

$$w = 3.7 \cdot 10^6 e^{-\frac{21000}{RT}} \text{ mole \%} \cdot \text{sec}^{-1}.$$

It follows from the foregoing that further kinetic studies of gas-phase oxidation by chromatographic methods may prove profitable.

The experimental results obtained cannot be finally explained in the light of the classical theory of chain-reaction kinetics. It is important to note that the fact that the reaction rate remains constant up to  $\sim 50\%$  conversion means that the reaction chain length is also constant. According to Semenov [8], the length of the steady-state chain in such cases "does not depend on the existing concentration at the given instant, but 'remembers' the initial concentration and is determined by it."

In the light of recent theories [13] it seems likely that the process rate is determined by a secondary, metal-free product (or group of products) formed during the initial macroscopic stage of catalyst conversion.

#### SUMMARY

1. Variations of the rate of hydrocarbon conversion with the degree of conversion in liquid-phase oxidation were studied in the oxidation of n-tridecane, n-tetradecane, and synthine; it was found that over a considerable part of the reaction the conversion rate is independent of the change of concentration of the starting material.

2. Cetyl alcohol did not have an inhibiting effect when introduced into the original tetradecane.

3. The activation energies for the oxidation of tetradecane in presence of Mn stearate in the initial stage (24 kcal/mole) and the stable stage (21 kcal/mole) were determined.

4. The experimental data were obtained by direct determinations of the residual unreacted hydrocarbons in the course of the reaction; their contents were found by adsorption chromatography on silica gel.

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\*\*\*Original Russian pagination. See C.B. Translation.

# COMPATIBILITY AND VOLATILITY OF PLASTICIZERS, AND GENERAL CONCLUSIONS\*

Sh. L. Lel'chuk and V. I. Sedlis

If a plasticizer is to be highly effective for polyvinyl chloride (PVC), it should be of aliphatic structure if possible. It is found in practice, however, that this creates definite limitations, because aliphatic plasticizers have an inadequate or limited solvent effect on polyvinyl chloride; in other words, they have poor compatibility with it.

In the use of any plasticizer, not only its effectiveness but also its compatibility with a given polymer must be taken into consideration. Plasticizer-polymer incompatibility results in exudation of the plasticizer and phase separation (demixing), especially under the action of heat and pressure, and in migration of the plasticizer to the surface.

Several methods were used for investigations of the compatibility of PVC with various plasticizers.

1) The method based on determinations of changes in the specific viscosity of the solution with the polyvinyl chloride concentration. Since PVC has poor solubility in the plasticizers studied, and only undergoes limited swelling at room temperature, a mixture of 50% (volume) of dichloroethane and 50% of plasticizer was used as the solvent for the specific-viscosity determinations. It was to be expected that the plasticizer molecules would interact both with the dichloroethane solvent and with the polymer, and the changes appearing on the  $\eta_{sp}/C = f(C)$  curve, where C is the PVC concentration, would depend on the interaction forces between the plasticizer and polyvinyl chloride, i.e., on their compatibility [1].

The graphs were used to determine the intrinsic viscosities  $[\eta]$  and the slopes of the straight lines. The greater the compatibility, the higher is the viscosity of the standard solution and the steeper the curve. These values for the 8 plasticizers studied are given in Table 1.

TABLE 1

Compatibility of PVC with Plasticizers, Determined by Different Methods

Plasticizer	Intrinsic viscosity $[\eta]$	tangent of angle of inclination	Precipitation threshold (cc methanol precipitant)	Swelling (%)	Dissolving temperature ( $^{\circ}$ C)	Polarity number $M_p/M$
Diethyl phthalate (DEP)	0.57	DEP 0.28	DEP 1.65	DEP 300	DEP 98	DEP 0.996
Tricresyl phosphate (TCP)	0.50	DBA 0.27	TCP 1.55	DBA 128	TCP 108	DBA 0.941
Dibutyl adipate (DBA)	0.48	TCP 0.26	DBA 1.45	DBP 120	DBA 110	DBP 0.816
Dibutyl phthalate (DBP)	0.40	DBP 0.23	DBP 1.40	TCP 80	DBP 117	TCP 0.268
Dioctyl phthalate (DOP)	0.30	DOP 0.18	DOP 1.10	DOP 35	DOP 120	DBS 0.254
Dibutyl sebacate (DBS)	0.17	DBS 0.15	DBS 0.90	DBS 22	DBS 130	DOA 0.237
Dioctyl adipate (DOA)	0.05	DOA 0.13	DOA 0.85	DOA 0.8	DOA 150	DOP 0.225
Dioctyl sebacate (DOS)	0.02	DOS 0.08	DOS 0.73	DOS 0.7	DOS 158	DOS 0.206

\*Communication IV in the series on the influence of plasticizers on the properties of polyvinyl chloride.

2) Determination of the temperature at which PVC dissolves in the plasticizer. The results depend on the rate of temperature increase and the PVC concentration; this is not an accurate method.

3) Determination of the solvent power of the plasticizer, by precipitation of PVC by a nonsolvent, methyl alcohol, from solution, i.e., by estimation of the precipitation threshold of PVC in plasticizer solution at room temperature under standard conditions.

The plasticizers tested are arranged in Table 1 in order of decreasing compatibility as determined by each of these methods, and the corresponding values are given.

Solvent power is often measured in terms of the amount of diluent or nonsolvent necessary to commence precipitation of the polymer from a clear solution. A plasticizer with good compatibility toward PVC requires a larger amount of nonsolvent to start precipitation of the polymer from a solution of standard concentration (0.2 g/100 cc in our experiments) than a plasticizer of poor compatibility. We consider that this method is sufficiently accurate, and that it achieves the desired aim. The results are given in Table 1.

4) Determination of the percentage swelling of PVC in the plasticizer at elevated temperatures (90° in our experiments). This temperature is close to the dissolving temperature for some of the plasticizers, and somewhat below it for others. This temperature was chosen because no significant decomposition of polyvinyl chloride occurs at 90°. The results are given in Table 1.

5) Because of the presence of the strongly polar C-Cl group in polyvinyl chloride, a condition for compatibility is considerable polarity of the solvent and plasticizer. Plasticizer polarity was expressed in terms of the fraction of polar groups in the molecular weight of the plasticizer, i.e., the  $M_p/M$  ratio, which we term the "polarity number," where  $M_p$  is the molecular weight of the polar groups and  $M$  is the molecular weight of the plasticizer. Thus, the most compatible plasticizers, DEP and DBA, have the highest polarity numbers (0.396 and 0.341). The least compatible plasticizer, DOS, has the lowest polarity number (0.207). The results are given in Table 1.

It is seen from the data in Table 1 that the compatibility characteristics determined by different methods are in general agreement: plasticizers with good compatibility with PVC have higher intrinsic viscosities, higher slope factors, require most precipitant for the start of precipitation, dissolve at the lowest temperatures, show the greatest percentage swelling at 90°, and have high polarity numbers; the reverse is true of plasticizers of poor compatibility. The compatibility sequences given by the first four methods almost coincide, apart from some minor transpositions of one or two members of the series. The sequence in order of polarity numbers shows appreciable deviations; this is because polarity is not the decisive condition for compatibility. The distance between the polar groups probably also has a certain influence here.

The following general conclusions may be drawn from the results given in Table 1.

1. Aliphatic plasticizers, which are dialkyl esters of aliphatic dicarboxylic acids, with the highest effectiveness toward PVC [2], are less compatible with it than plasticizers containing aromatic groups; this is confirmed by practical experience.

2. The compatibility of a plasticizer with PVC decreases with increasing length of the hydrocarbon portion of the molecule (for example, compare DBA with DOA, DBS with DOS, and DEP with DOP).

3. Increase of the plasticizer polarity (increase of the proportion of polar groups in the molecular weight of the plasticizer) increases its compatibility with PVC but lowers its effectiveness.

Thus, the aliphatic portion of the plasticizer molecule exerts opposing influences with regard to compatibility and effectiveness. For high effectiveness, a plasticizer with a large aliphatic portion is required, whereas for better compatibility a strongly polar plasticizer with a small aliphatic portion is needed. It is very difficult, perhaps impossible, to satisfy both these requirements simultaneously. The problem can be solved either by a compromise, with the use of a plasticizer the structure of which partially satisfies both requirements, or by the use of mixtures of plasticizers from the two classes, as is often done in practice.

In addition to compatibility and effectiveness, there is a third important requirement for plasticizers — low volatility, which largely determines the constancy of the technical properties of the product, and its service life. If a plasticizer is highly volatile, a considerable proportion is lost by evaporation during use; the material

"ages," and becomes hard and brittle. In Table 2 the plasticizers are arranged in order of increasing volatility the values for the pure plasticizers being given. The volatility of a plasticizer was determined as the percentage loss in 6 hours at 100° under standard conditions (in vessels of equal size, with equal surface areas, heights of the liquid column, and rates of temperature increase).

The relative volatilities of the plasticizers, that of tricresyl phosphate being taken as unity, are also given in Table 2.

It follows from Table 2 that the least volatile plasticizer (apart from polymeric plasticizers) is tricresyl phosphate. This, together with its good compatibility with PVC, is a great advantage, as it can be used in high concentrations, and therefore, despite its low effectiveness, it is very suitable for a number of important technical purposes, as was demonstrated by us earlier [2].

The most volatile plasticizer is diethyl phthalate, which is hardly ever used as a plasticizer for PVC.

As is to be expected, plasticizer volatility decreases with increase of molecular size.

TABLE 2  
Plasticizer Volatility

Plasticizers	Volatility (% loss in 6 hours at 100° and normal pressure	Relative volatility
TCP	0.06	1.0
DOS	0.07	1.2
DOP	0.09	1.5
DOA	0.45	7.5
DBS	0.46	7.7
DBP	0.57	9.5
DBA	0.79	13.2
DEP	1.20	20.0

It must be pointed out that our volatility figures refer to the pure plasticizers and do not fully represent their behavior in plasticized compositions. The compatibility with the polymer must also be taken into account. A plasticizer of low volatility but poor compatibility is retained badly in the composition, especially at high concentrations, and tends to migrate, i.e., to pass to the surface, which naturally facilitates and intensifies evaporation. This effect is especially prominent in articles with large surface areas relative to thickness (such as films, varnish or lacquer coatings, cable sheaths, etc.).

It is for this reason that a more costly and scarce plasticizer such as dioctyl phthalate, which has satisfactory effectiveness and compatibility and very low volatility, has displaced the volatile dibutyl phthalate, which was formerly used very extensively, in almost all high-quality products.

#### General Conclusions Concerning the Interaction of Plasticizers with PVC

Polyvinyl chloride is a particularly suitable material for studies of plasticizer-polymer interaction, as it reveals especially clearly the influence of plasticizers on the physical, mechanical, and electrical properties of polymers, in conferring rubberlike properties to a hard, rigid, brittle, and high-melting material.

On the basis of earlier results [2, 3] it is possible to draw a number of more general conclusions concerning the interaction of plasticizers with PVC.

The high glass-transition temperature of polyvinyl chloride, the high temperature range of its plastic deformation, its very slight high-elastic deformation at normal temperatures, and low solubility in ordinary solvents



and plasticizers, are generally attributed to the existence of large intermolecular and intramolecular forces (rigidity, low mobility of the PVC chains and chain segments), which in its turn is the result of the presence of a large number of strongly polar C-Cl groups, with a high dipole moment, in the PVC macromolecule. However, these forces act only at very short distances and diminish rapidly with the distance, in inverse proportion to the 4th and 6th power of the distances; i.e., the forces are proportion to  $1/r^4$  and  $1/r^6$ . Thus, if the distance between the PVC chains is halved, the intermolecular forces are reduced roughly 32-fold and 64-fold. The action of a plasticizer can be schematically represented as follows: the plasticizer molecules penetrate between the polymer macromolecules, push them apart, solvate them, separate the interacting groups, shield the polar groups, disturb the regularity and order of the polymer macromolecules, and thereby greatly weaken the intermolecular and intramolecular forces and increase the mobility of the polymer molecules and chains.

In accordance with this mechanism, increase of the length, volume, and size of the plasticizer molecule should increase its effectiveness; this is confirmed by the results of our investigations and is observed in practice (DOS is more effective than DBS, DOP is more effective than DEP and DBP). On the other hand, if the plasticizer molecule is large, its mobility is decreased, it penetrates with greater difficulty between the PVC macromolecules, and the solvation and compatibility with the polymer are diminished; this is likewise confirmed by experiment and practical experience (DEP is more compatible with PVC, and causes greater swelling of the latter, than DBP and DOP; the same is true for DBS and DBA as compared with DOS and DOA). Many workers have noted the relationship between solvation and molecular dimensions and shape [4].

TABLE 3  
Principal Properties of Plasticizers

Plasticizer	Effectiveness E (*)	Compatibility (swelling, with TCP = 1)	Relative volatility (volatility of TCP = = 1)
TCP	9.4	1	1
DEP	9.8	3.75	20
DBP	10.6	1.50	9.5
DOP	11.9	0.438	1.5
DBA	12.4	1.60	13.2
DOA	13.1	0.01	7.5
DBS	13.8	0.275	7.7
DOS	15.1	0.0087	1.2

Weakening of the intermolecular forces and increase of chain and segment mobility should diminish the strength and increase the extensibility of the polymer, increase ion mobility and electrical conductivity and thus lower the resistance of the polymer; it should favor the formation of temporary channels in the composition which allow the passage of water molecules, and thus increase the diffusion of water and moisture permeability. All these effects should be intensified with increased effectiveness of the plasticizer. Regular linear relationships between these properties and plasticizer effectiveness were discovered by our investigations and expressed as empirical quantitative formulas which give good agreement with experimental results [3, 5].

Our results and the relationships established from them have been used to characterize the plasticizers tested, in terms of numerical values of three fundamental properties: the effectiveness (effectiveness number E), compatibility (swelling value and relative swelling), and volatility (relative volatility).

It was shown that in the case of copolymers our principles and method can be applied to yield interesting results, if copolymerization of monomers with rigid segments is regarded as internal plasticization.

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## INVESTIGATION OF THE CHEMICAL COMPOSITION OF WOODS BURIED IN PEAT DEPOSITS

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Theories of the origin of solid fossil fuels are largely founded on the composition of the final decomposition products of the original plant materials, the composition of which is assumed to correspond to that of plants known at the present time.

Apart from the fact that this assumption is highly tentative since it cannot be verified, the decomposition products have in most cases lost even the most remote resemblance to the original materials, either completely, as in the case of coals with rare exceptions of lignites, or partially, as in the case of peats. However, even in the latter case, when the nature of the plant deposit can be accurately established, the relative participation of each plant species of the given group in the formation of the organic fuel mass remains unknown, as the rates of their biochemical decomposition may have differed despite the same external conditions. Therefore studies of a particular example of decomposition of definite plants under natural conditions are significant in determination of the character of the natural process as a whole. Peat deposits contain, for thousands of years, remains of wood of different degrees of decomposition, in the form of fairly large lumps, which for various reasons escaped total decomposition.

The existing published data refer mainly to buried residues of pine wood; it is generally reported that its resin content increases [1]. The information with regard to other components is contradictory. For example, Rakovskii and Vysotskaia [2] gave analytical results for pine wood 1000 to 2000 years old, according to which not only the lignin, but even the cellulose and hemicellulose contents changed very little in comparison with fresh wood [2]. On the other hand, Skrigan found that the carbohydrate content of pine wood decreased and the nonhydrolyzable residue increased with age. However, his graph for the contents of the individual components does not reveal these changes for ages up to 2000 years. They become more or less noticeable only during the third thousand years [3].

The present paper deals with a study of four woods aged 1300-2000 years; pine (two samples), birch, and willow, found in different peat deposits (Table 1).

The group analysis of the woods was performed in the following sequence: benzene extraction, boiling water treatment (3 times), treatment with 1.0 N hydrochloric acid on a boiling water bath for 5 hours, extraction with 0.1 N caustic soda, the same on the water bath to total extraction of humic acids, extraction with alcohol-benzene mixture, treatment with 72% sulfuric acid for hydrolysis of cellulose and isolation of nonhydrolyzable residue, generally taken as lignin. This procedure differs from the usual analytical procedure for fresh wood in the following respects.

- 1) The wood was extracted with caustic soda to determine the nature of the humification of the original organic material. Living plant material also contains components extracted by alkali, but in the usual analytical procedure they are found in different fractions of the plant compounds.

The alkaline extract was treated with hydrochloric acid to separate the substances soluble in it from the insoluble humic acids. The content of the insoluble substances was found from the difference between the weight

of the original sample and the sum of the insoluble humic acids with the residue after the caustic soda extraction.

TABLE 1

Samples of Wood From Different Peat Deposits

Sample No.	Wood	Type of peat	Depth of sample (m)	Degree of decomposition of peat (%)	Peat origin
1	Pine	Upper, medium sphagnum	1.1	20	Veliki Mokh, Mogilev province
2	Pine	Upper, pine-cotton grass	1.3	55-60	Vasil'kovskoe, Kalinin province
3	Birch	Lowland, forest	1.0	45-50	Kosino, Moscow province
4	Willow	Lowland, wood-forest	1.0	45-50	Mikhnevskoe, Moscow province

2) Extraction with alcohol-benzene mixture was performed after extraction of the humic acids, in order to remove residual bitumens and the products of carbohydrate conversion which are soluble in this mixture [4]. As will be clear from the data below, this step is fully justified, as otherwise the alcohol-benzene fraction would be in the nonhydrolyzable residue and would introduce considerable error into the analytical results.

TABLE 2

Analytical Data for 4 Wood Samples (in percentages on the organic mass)

Components	Number of wood sample			
	1	2	3	4
Ash, on the bone-dry wood	0.22	0.17	4.28	4.75
Benzene-soluble substances	2.83	46.93	13.52	1.41
Water-soluble substances	1.01	Nil	1.12	11.42
Substances hydrolyzed by 1.0 N hydrochloric acid	13.88	8.73	8.68	17.33
Insoluble humic acids	0.96	1.21	9.40	9.29
Substances insoluble in acid and alkali	9.29	6.06	5.83	10.13
Substances soluble in alcohol-benzene mixture	3.17	2.34	6.82	1.49
Cellulose	41.39	22.35	6.93	6.45
Nonhydrolyzable residue	27.95	13.53	48.78	42.48
Reducing substances	14.02	8.90	7.75	11.16
Uronic acids	8.18	7.17	8.62	6.28
Pentosans	2.67	1.24	0.54	1.60
Total methoxyl	5.19	2.69	3.79	6.18
Nonhydrolyzable methoxyl	4.23	2.03	2.89	5.09
Hydrolyzable methoxyl	0.96	0.66	0.90	0.09

The amount of substance hydrolyzed by 1.0 N hydrochloric acid was found from the difference in weight between the samples before and after the hydrochloric acid treatment, with the ash content taken into account. All the other determinations were performed by the methods used previously [2]. The analytical results for the wood are summarized in Table 2.

Literature data on the compositions of fresh woods are contained in Table 3.

Comparison of the two sets of analytical data suggests that samples of buried wood can be classified in two types by the changes in their chemical composition: those found in upper and lowland peat deposits respectively.

It is known that lowland peats are deposited in conditions of increased aqueous mineral feeding. Therefore, they are rich in ash and have  $\text{pH} \geq 7$ . Upper peats have low ash contents, and  $\text{pH} < 7$ . Their moisture contents vary in fairly wide limits. There is no doubt that differences in the aqueous mineral conditions must influence the conversion of the vegetable residues; this is confirmed by the increased ash contents of birch and willow woods. Their carbohydrate contents were consumed to a much greater extent than in the two pine samples from upper deposits. At the same time, their contents of unhydrolyzable residue greatly increased, and 15-20% of an alkali-soluble fraction was formed, including over 9% of humus substances. In addition birch wood was much enriched with compounds soluble in benzene and alcohol-benzene mixture, totaling 20.34%. An increase of these fractions is also found in pine No. 2, 49.27%. The elementary composition of the benzene-soluble bitumens of both woods, calculated on the organic mass, was: birch C 78.46%, H 10.40%; pine No. 2 C 78.95%, H 9.23%. The resin content was determined by ether extraction: in birch bitumen, 45.16%, in No. 2 pine bitumen, 91.84%. An increase in the amount of ether extract was noted previously for pine by Rakovskii and Vysotskaia, but not to such a high level [2].

TABLE 3  
Literature Data on the Composition of Fresh Wood

Components	Percentages on bone-dry wood		
	pine [6]	birch [6]	willow [7]
Ether extract	2.00	1.34	1.23
Alcohol extract	—	—	2.22
Aqueous extract	—	—	1.42
Hemicelluloses	28.43	42.00	24.27
Cellulose	40.97	34.01	46.26
Lignin	27.80	21.21	28.42
Uronic acids	2.80	4.01	—
Pentosans	10.50	22.01	24.70
Total methoxyl	4.55	5.97	5.56 *
Nonhydrolyzable methoxyl	4.05	3.80	3.78 *
Hydrolyzable methoxyl	0.50	2.67	1.78 *
Ash	0.20	0.35	0.24 *

\* In absence of literature data, ash and methoxyl were determined in a sample of *Salix fragilis* from the Moscow region.

However, Karavaev and Matveeva also found a high bitumen content, up to 37.73% [8], in certain lignites, while in bitumen from Southern Ural lignite they found resins only, waxes being entirely absent [9]. Thus, the above-mentioned conversions of wood, especially of pine No. 2, may be regarded as characteristic with regard to the benzene-soluble substances. Analysis of pine No. 1 revealed only slight changes in the principal components — cellulose, unhydrolyzable residue — and in methoxyl content, as compared with fresh wood. Its difference from the greatly changed pine No. 2 is probably due, not to the relatively small age difference, about 300 years, but to the fact that sample No. 1 came from sphagnum peat; it is known that sphagnum is more resistant than many other peat-formers to biological destruction factors [5]. The elementary composition of woods, debittumenized by means of benzene, is given in Table 4.

It seems likely that the reason for the higher contents of C and H in birch wood is its higher content of bitumen, extracted by alcoholic benzene, as compared with the other woods (Table 2). The isolated humic acids and nonhydrolyzable residues were investigated by the usual method; the hydroxyl groups were methylated

by means of dimethyl sulfate in alkaline solution in a current of nitrogen, and the carboxyl groups, by means of methanol in hydrochloric acid. Methoxyl groups were determined by a method of Viebock and Schwappach. The analytical results are given in Table 5.

TABLE 4

Elementary Composition of Wood after Removal of Benzene-Soluble Substances (percentages on the organic mass)

Sample No.	C	H
1	52.19	5.92
2	52.06	5.85
3	63.11	6.84
4	57.29	5.49

The elementary composition found for the humic acids is not typical for humic acids from peat and brown coal, which usually contain 58.6 and 59.5% C and 4.9 and 4.5% H [10]. The high initial methoxyl and low contents of acidic groups are also uncharacteristic of true humic acids [11]. The isolated humic acids are rather nearer to the unhydrolyzable residues in their degree of oxidation, and in the case of wood from pine No. 2 and willow they are even considerably more reduced than the latter. By their composition they are closer to the hymatomelanic acids studied by one of us earlier [11]. The following was found in the analysis of the product isolated from No. 1 pine wood: its methoxyl number was decreased to less than one half of the original

value on methylation with dimethyl sulfate in 20% caustic soda solution, but the initial level was restored almost completely by the action of methanol. Consequently this substance must be entirely devoid of free carboxyl and hydroxyl groups, which are fully methylated even in the natural state.

TABLE 5

Analyses of Humic Acids and Nonhydrolyzable Residues (percentages on the organic mass)

Sample No	Elementary composition			Methoxyl numbers			
	C	H	O + N	initial methoxyl	ether methoxyl	total methoxyl	ester methoxyl
Humic acids							
1	62.99	7.48	29.53	9.68	4.02	9.12	5.10
2	66.01	6.62	27.37	7.89	—	—	—
3	65.47	7.34	27.19	5.03	10.79	15.11	4.92
4	59.39	5.48	35.13	6.24	15.91	18.91	3.00
Nonhydrolyzable residues							
1	65.84	5.45	28.71	14.80	21.62	22.84	1.22
2	54.11	5.58	40.31	14.26	—	—	—
3	66.27	7.01	26.72	4.95	9.94	12.93	2.99
4	56.75	4.95	38.30	12.95	21.76	22.37	0.61

Thus, the compounds isolated by means of alkali and insoluble in acids cannot be classified as true humic acids, and probably represent an intermediate stage in the formation of the latter from various plant components. With regard to the nature of the nonhydrolyzable residues, it must be noted that some of them, such as those from woods Nos. 2 and 4, cannot be considered as true lignins, because of their low carbon contents. As already stated, the conversions undergone by woods buried in different peat deposits differ in character. This is confirmed by analysis of the nonhydrolyzable residues. In the case of the two pine samples, taken from upper deposits, residue No. 1 was virtually without any quantitative or qualitative change. The yield of residue No. 2, and the number of nonhydrolyzable  $\text{OCH}_3$  groups of the wood, were halved, but the nonhydrolyzable residue was itself not demethylated, as its methoxyl number is 14.26%, whereas for lignin of fresh pine it is 14.01%, as shown by calculations based on the amount of nonhydrolyzable methoxyl. In this case the lignin, and also all the substances forming the nonhydrolyzable residue as a whole, were undoubtedly split uniformly. On the other hand, as already noted in woods contained in lowland peats, the contents of nonhydrolyzable residues increased considerably: by a factor of 2.3 for birch, and about 1.5 for willow. These results can be ascribed to



actual increases of the amounts of substances entering the corresponding fractions. This is confirmed by the changes in their methoxyl numbers. The  $\text{OCH}_3$  group content in the lignin of fresh birch, according to the unhydrolyzable methoxyl content, is 11%, whereas for the buried wood residue it is 4.95%; i.e., the methoxyl number decreased 2.2-fold. However, this demethylation of the lignin is in fact only apparent, as it is not caused by conversion of the lignin itself, but by the entry of corresponding amounts of nonhydrolyzable substances, newly formed from other wood components, into the lignin fraction. The actual unhydrolyzable methoxyl content of the birch sample (2.89%) differs very little from that of the fresh wood (3.30%). The unhydrolyzable  $\text{OCH}_3$  groups, in the case of buried birch, merely became distributed between the alkali-soluble and alkali-insoluble fractions. The former contained 16.26%, and the latter 83.74% of the total nonhydrolyzable methoxyl.

Birch wood lost, in fact, only the easily hydrolyzable  $\text{OCH}_3$  groups, the contents of which fell by 2/3, but these were not part of the lignin. Although the content of the willow-wood residue also increased, analysis showed that plant material may undergo a different type of conversion: the methoxyl number remained almost unchanged, being 13.34% for fresh and 12.95% for buried wood.

On the whole, however, the unhydrolyzable methoxyl content greatly increased in this case because this wood contains virtually no substances with easily hydrolyzable  $\text{OCH}_3$  groups: all the methoxyl groups in willow were distributed between humic acids (9.52%) and nonhydrolyzable residue (90.48%).

Therefore these two fractions, formed by the decomposition of vegetable matter, are genetically closely related. The question of the conversion of methoxyl-containing compounds is of great importance in principle, as there is a belief that plant lignin is demethylated only under anaerobic decomposition conditions, while in aerobic conditions the whole molecule is split while the  $\text{OCH}_3$  group content remains unchanged [12]. The analytical data in our paper do not suggest that lignin demethylation is the principal characteristic of the decomposition of the woods studied. Demethylation was observed in only one instance (in the analysis of birch), but to a very small extent, which can hardly have any significance in determining the process conditions, especially as all the woods, which were taken from a depth of about 1.0 meter in the deposits, were similarly situated with regard to aeration. Moreover, the modern theory of peat formation does not attribute any important role to anaerobic organisms in the process [13]. The course of biochemical decomposition of plant residues is still very obscure.

The buried wood samples were supplied by A. I. Shatenev, and fresh willow by K. K. Lebedev, to whom we express our gratitude.

#### SUMMARY

In a study of 4 woods buried in peat (samples of pine, birch, and willow) it was found that the nature of the decomposition varies with the nature of the wood, its location in upper or lowland deposits, and the kind of peat in a given type of deposit.

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## HYDROGENATION OF GLUCOSE IN PRESENCE OF POWDERED RANEY NICKEL CATALYST IN FLOW CONDITIONS\*

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Despite the high activity of Raney nickel catalysts, they have certain disadvantages inherent in all alloy catalysts used industrially in granulated form, where the active surface layer becomes deactivated during hydrogenation.

This effect is especially pronounced in the hydrogenation of aqueous sugar solutions containing impurities, which are deposited on the catalyst in varying amounts, according to the quality of the solution. Therefore, it becomes necessary to carry out alkaline regeneration of the catalyst at fairly frequent intervals in order to maintain its activity at the required level.

However, steady and regular operation cannot be maintained by this means, even in the intervals between regenerations, because of the gradual decrease of catalyst activity.

As was noted earlier [1], Zardalishvili, Tursin, and Tsyplakov [2] took out, in 1943, the first patent for a process for the continuous hydrogenation of glucose in presence of a stationary catalyst. Subsequently Lolkema, Veugter, and Weston [3], and Kasehagen [4], modified the process somewhat; in their modifications, a mixture of glucose solution and the suspended catalyst was passed through the reactor. These experiments were performed in presence of supported nickel catalyst.

Apart from these patents, which are of a descriptive and advertising character, the question is not considered in the general literature. Studies of the continuous hydrogenation of glucose in presence of a moving catalyst were therefore of interest. The glucose was hydrogenated in presence of chromium-promoted Raney nickel catalyst.

### EXPERIMENTAL

Effect of the amount of catalyst. To determine the influence of the amount of catalyst on the degree of hydrogenation of glucose, laboratory experiments were carried out on the hydrogenation of 16% glucose solution in presence of 1, 2, and 3 g of catalyst respectively (calculated as the alloy). Each portion of catalyst was used in the hydrogenation of 3-4 portions of glucose solution. The experimental procedure was described earlier [1]. The conditions were: hydrogenation time 1 hour, temperature 120°, pressure 60 atm, volume of glucose solution 100 ml, concentration of glucose solution 16%. The results are given below and plotted in Fig. 1.

The results show that the necessary degree of hydrogenation of the glucose (99%) is attained under these conditions with the use of 2 g of catalyst, i.e., 12.5% calculated on the glucose.

The possible use of activated carbon as support. Most monographs on catalysis [5] contain numerous recommendations concerning the use of carbon as a support in the hydrogenation of organic compounds.

\* Communication II.

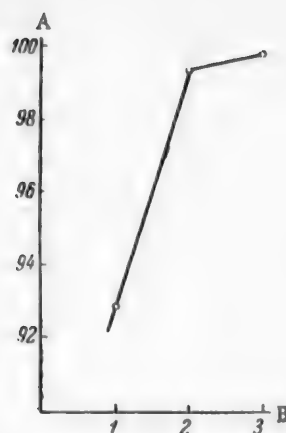


Fig. 1. Effect of the amount of catalyst on the degree of hydrogenation of glucose. A) Amount of glucose hydrogenated (%), B) amount of catalyst (g).

Amount of catalyst (g)	Amount of glucose hydrogenated (%)
1•	92.90
	85.00
	76.00
	71.95
2•	99.4
	99.07
	98.85
3•	99.81
	99.62
	99.46
	99.10

Accordingly, experiments were carried out on the influence of various types of activated carbon on glucose hydrogenation under the following conditions:

hydrogenation time 1 hour, temperature 100°, pressure 60 atm, 1 g catalyst + 3 g carbon, pH = 8.5. The supports tested were "B" grade carbon, "kollaktivit" and sulfonated coal. The results are given below.

Type of carbons	Amount of glucose hydrogenated (%)
"kollaktivit" • •	27.9
	22.9
Sulfonated coal • • •	33.9
	27.9
	25
	20.3
"B"	44.2
1 g of catalyst without carbon	79.0

These results indicate that the catalyst activity at 100° is reduced by the addition of carbon. The least decrease of activity was found in presence of carbon "B". An attempt was made to solve the problem by hydrogenation of glucose at higher temperatures. The experiments were performed in presence of carbon "B" at 120, 130, and 140°. For comparison, experiments in presence of 1 g of catalyst without carbon were also carried out.

The results are given on the next page and plotted in Fig. 2.

It follows from these results that if the process temperature is raised to 130-140°, the catalyst activity is virtually the same with and without added carbon.

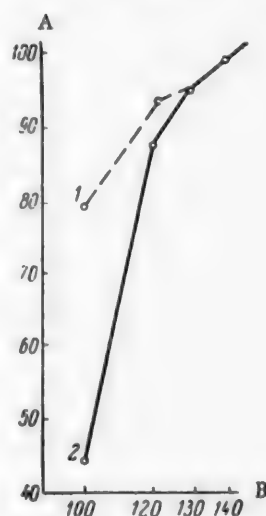


Fig. 2. Effect of temperature on the degree of hydrogenation of glucose. A) Amount of glucose hydrogenated (%), B) temperature (°C). 1) 1 g catalyst, 2) 1 g catalyst + 3 g carbon.

- A single portion of catalyst for all the experiments.
- • One portion of catalyst for two experiments.
- • • One portion of catalyst for four experiments.

Catalyst charge	Temperature (°C)	Amount of glucose hydrogenated (hydrogenation time 1 hour, P = 60 atm.) (%)
1 g catalyst + 3 g carbon "B"	120	87.4
1 g catalyst without carbon	120	92.9
1 g catalyst + 3 g carbon "B"	130	95.1
1 g catalyst without carbon	130	95.3
1 g catalyst + 3 g carbon "B"	140	99.06
1 g catalyst without carbon	140	98.8

Effect of catalyst dispersity on its activity. Experiments were carried out in order to study the effect of dispersity on the activity of the catalyst.

The aluminum-nickel alloy was ground\* in a vibratory mill with a No. 3 steel body, 11 dm<sup>3</sup> in volume, mounted on springs, vibrating at 2900 vibrations per minute. This alloy taken for grinding was in the form of granules, 1-4 mm in size, of bulk density 2 kg/liter. Steel balls 10-12 mm in diameter were used for the grinding; the total ball volume was 8.8 dm<sup>3</sup>, or 80% of the mill volume. The material was ground for 15 minutes, 1.5 liters of distilled water was added, and the grinding was continued for 60 minutes. Samples were taken during the grinding to determine the influence of the duration of vibratory grinding on the specific surface of the alloy. The results are given below and in Fig. 3.

Grinding time (minutes)	Specific surface, by Tovarov's method [6] (in cm <sup>2</sup> /g)
3	1710
9	3020
12	3300
15	3490
20	4350
25	4960
30	5600
81	12200

The powders of different dispersity were tested for relative activity by the method described earlier [1].

The results of experiments on the effect of dispersity on the alloy activity with hydrogenation time 1 hour, temperature 120°, pressure 60 atm., and 1 g of catalyst per 100 ml of 16% glucose solution are given below.

Specific surface (cm <sup>2</sup> /g)	Amount of glucose hydrogenated (%)
4350	96.2
5620	94.8
12200	94.1

It is seen that the catalyst activity does not depend on its dispersity. For comparison, the effect of particle size on catalyst activity was investigated under the same conditions. The results are given on the next page.

These last two series of experiments demonstrate a sharp difference in activity between powdered and granulated catalysts, whereas Rapoport and Sil'chenko [7] found that in the hydrogenation of phenol the degree of subdivision of the Raney catalyst, in the range from a powder to 2.5 mm grains, has almost no effect on the catalyst activity.

\* We thank N. E. Levina for grinding the alloy.

Granule size (mm)	Amount of glucose hydrogenated (%)
0.25	86.6
1-2	51.2
3-5	11.2

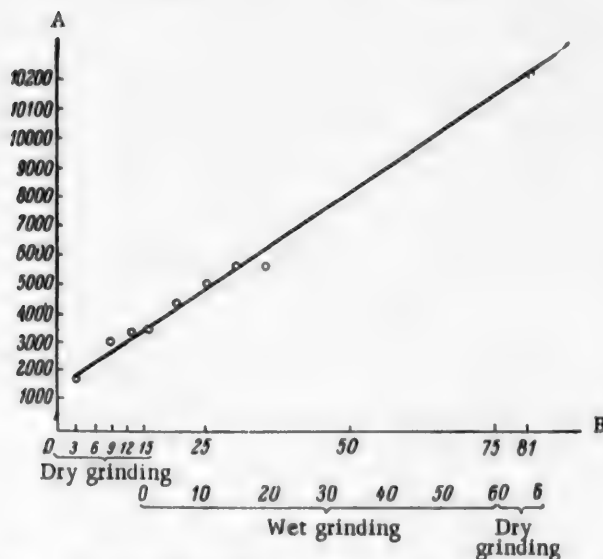


Fig. 3. Effect of grinding time on specific surface. A) Specific surface, by Tovarov's method ( $\text{cm}^2/\text{g}$ ), B) time (minutes).

**Experiments in a continuous unit.** The experiments were performed in presence of moving Raney nickel catalyst, promoted with chromium, at  $135^\circ$  and 70 atm. The mixture of glucose solution and catalyst was adjusted to pH = 8.5. The glucose concentration was 20%, the specific surface of the catalyst was  $12200 \text{ cm}^2/\text{g}$ , and 10% of catalyst on the weight of glucose was used. The apparatus is shown schematically in Fig. 4.

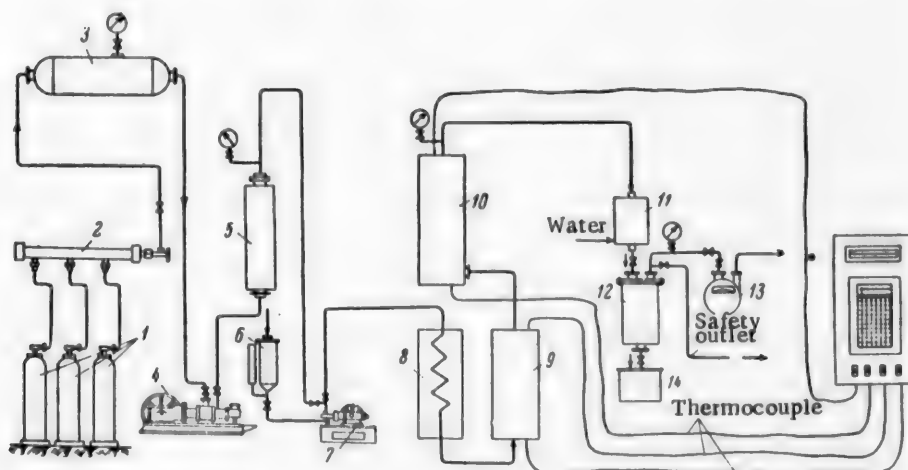


Fig. 4. Continuous unit for hydrogenation in presence of Raney nickel catalyst. Explanation in text.

Hydrogen from the cylinders 1 enters the hydrogen ramp 2, and then passes through a reducing value into the gas holder 3. From the gas holder it passes at 1-1.5 atm into the compressor 4, where it is compressed to 300 atm, and enters the general system through the buffer vessel 5.



The mixture of glucose solution and dispersed catalyst is poured into the receiver 6, and is pumped by means of pump 7, with continuous stirring, into the heater 8, where it is preheated, then passes into the first and second reactor, 9 and 10, and then enters the separator 12, where the hydrogen is separated from the solution, by way of the condenser 11.

The hydrogen passes through the gas meter 13 and escapes into the air. The liquid containing the dispersed catalyst is removed as it accumulates in the separator, through a throttle valve into the receiver 14, open to the atmosphere.

The results of the autoclave experiments show that the catalyst activity diminishes after hydrogenation of the first portion of glucose. It was therefore necessary to determine the amount of fresh catalyst which should be added to the spent catalyst in order to restore its original activity. It was found that 10% of fresh catalyst must be added. Therefore, in the experiments with the continuous unit 10% of the spent catalyst was removed after each experiment, and replaced by 10% of fresh.

The results obtained in the continuous unit are given below.\* The conditions were: hydrogen feed rate 400 liters/hour, solution feed rate 1000 ml/hour, reactor volume 1000 ml.

Experiment No.	Amount of glucose hydrogenated (%)	Experiment No.	Amount of glucose hydrogenated (%)
1	99.92	7	99.91
2	99.87	8	99.36
3	99.85	9	99.82
4	99.81	10	99.00
5	99.74	11	99.74
6	99.13		

The results show that this addition of fresh catalyst is justified, as the degree of glucose conversion remained almost constant during 11 experiments.

#### SUMMARY

1. The hydrogenation of glucose solutions in presence of a moving powdered Raney nickel catalyst was studied in a continuous unit, and it was shown that the hydrogenation of glucose is virtually complete in 1 hour at 135°, hydrogen pressure 70 kg/cm<sup>2</sup>, with 10% of catalyst relative to the amount of glucose. The spent catalyst can be used in 10 more cycles provided that each time 10% of it is replaced by fresh catalyst.

2. It is shown that variations of the specific surface of the aluminum-nickel alloy in the 4350-12200 cm<sup>2</sup>/g range do not influence the catalyst activity; changes of the alloy particle size from 3-5 to 0.25 mm, and down to the powders of the above-named dispersities, have a significant influence on catalyst activity.

3. The catalyst activity is not affected by active carbon "B", sulfonated coal, or "kollaktivit" used as supports.

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\* Each successive experiment was performed with the catalyst from the preceding experiment, after replacement of 10% of spent catalyst with 10% of fresh.

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## CATALYTIC METHODS FOR THE PRODUCTION OF METHYL ISOBUTYL KETONE

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The higher homologs of acetone, ketones, could be widely used in a great number of branches of the national economy, if it were not for their high cost and scarcity, which are due to the lack of a convenient and cheap method of ketone production.

Special importance has been recently attached to their use as polar solvents in the separation of hydrocarbons by extractive crystallization with urea and thiourea [1] and in the deparaffinization of lubricants [2], where higher ketones are irreplaceable materials.

The development of an economical method for the production of higher ketones from available raw materials is a promising line of research.

The authors of this paper propose a method for the production of methyl isobutyl ketone and diisobutyl ketone from acetone and isopropyl alcohol, which are quite readily available as raw materials. In this connection mention should be made of a new process for the production of phenol from benzene and propylene, which is now extensively used, because about 600 kg of acetone is obtained as a by-product for each ton of phenol in this process [3].

The catalytic condensation of acetone to methyl isobutyl ketone, by a process developed by the authors [4], is described in this paper.

The physicochemical properties of acetone and methyl isobutyl ketone are compared below:

	Acetone [5]	Methyl isobutyl ketone [5]
Boiling point (°C)	56.2	118.0
Melting point (°C)	-94.9	-84.7
Density	0.7905 <sub>20</sub> <sup>20</sup> <sub>4</sub>	0.817 <sub>20</sub> <sup>20</sup> <sub>20</sub>
Vapor pressure at 20° (mm Hg)	181.0	11.3
Solubility in water at 20° (%)	∞	1.91
Solubility of water at 20° (%)	∞	2.81
Refractive index $n_D^{20}$	1.3591	1.3959

A reaction for the conversion of acetone into higher ketones was described by Hardy and Morgan [6]. The process occurs in two stages: 1) aldol condensation of acetone in presence of aqueous potash solution, and 2) hydrogenation of the condensation products at 150-160° and 120 atm over nickel or copper-barium-chromium catalyst. The reaction yielded methyl isobutyl ketone and 3,5,5-trimethylcyclohexanol-1.

Vapor-phase condensation of acetone in presence of solid alkaline catalysts [Ba(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, etc.] gave good yields of diacetone alcohol, which is readily converted into mesityl oxide by the action of dehydrating agents (iodine). Mesityl oxide can be obtained directly from acetone by the action of anhydrous alkalis on heating. Phorone, isophorone, and mesitylene are obtained as by-products with the mesityl oxide.

Lassier [7] hydrogenated acetone over a nickel catalyst at 200-300° and obtained about 30% of condensed products. These were shown to contain methyl isobutyl ketone and small amounts of diisobutyl ketone.

In a study of the catalytic conversions of ethyl alcohol over promoted copper catalyst [8, 9] the formation of mesityl oxide and methyl isobutyl ketone was demonstrated, and confirmed by experiments on the condensation of acetone in presence of hydrogen over the same catalyst [10, 4].

In suitable conditions, isopropyl alcohol can also be a convenient starting material for the production of higher ketones. Ipatieff, Gerstbein, and Pines [11] studied the decomposition of isopropyl alcohol over catalysts containing magnesium oxide, and found that at 490° the following were formed: acetone, propylene, mesitylene oxide, isophorone, liquid hydrocarbons, methyl isobutyl ketone, and diisobutyl ketone.

The present paper deals with a study of the catalytic conversions of isopropyl alcohol and acetone in presence of hydrogen over a copper catalyst promoted with thorium oxide [8, 12].

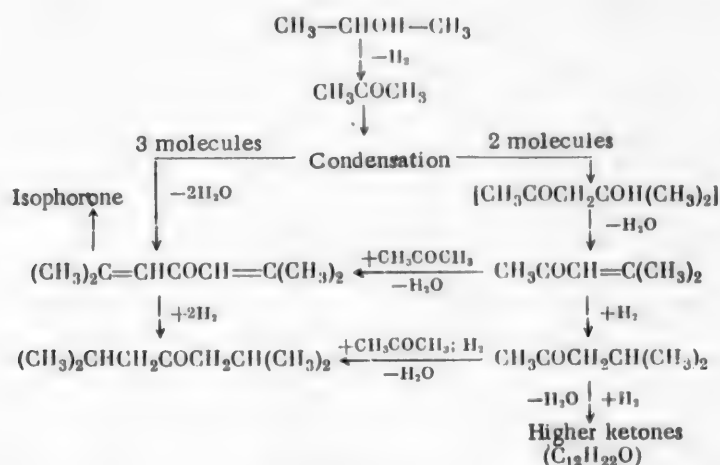
Methyl isobutyl ketone was formed in the vapor-phase catalytic condensation of acetone in presence of hydrogen. The optimum conditions for its formation are a temperature of 300-325°, and a space velocity of 500-600. The yield of methyl isobutyl ketone under these conditions is 20-28%, or 70-75% of the theoretical, calculated on the converted acetone. Diisobutyl ketone and other higher ketones are also formed under these conditions. Increase of the space velocity to 1000 at 300° results in a slight decrease of the methyl isobutyl ketone yield, and a sharp decrease of the yields of the higher ketones.

The catalytic conversion of isopropyl alcohol into methyl isobutyl ketone proceeds under the same conditions as those used for acetone, but it is not necessary to supply hydrogen. The yield of methyl isobutyl ketone is 60-65% of the theoretical.

Increase of the water content in the original isopropyl alcohol decreases the methyl isobutyl ketone content of the condensate, but the degree of conversion of the alcohol into the ketone remains constant because of decreased side reactions.

The condensates contain up to 65-70% unreacted acetone, which may be recycled together with hydrogen or with a fresh portion of isopropyl alcohol. In the latter case the alcohol is completely converted into acetone, and its presence favors the reaction of methyl isobutyl ketone formation.

The conversion of isopropyl alcohol and acetone into higher ketones may be represented as shown below:



## EXPERIMENTAL

The laboratory unit used for studies of the conversion of isopropyl alcohol and acetone into methyl isopropyl ketone was described in an earlier paper [8].

The starting materials were: 1) dry 98.6% isopropyl alcohol of b.p. 82-82.5°,  $n_D^{20}$  1.3775 (literature data: b.p. 82.4°,  $n_D^{20}$  1.3773) [13]; 2) acetone of b.p. 56-56.5°,  $n_D^{20}$  1.360 (literature data: b.p. 56.2°,  $n_D^{20}$  1.3591 [13]), and 3) hydrogen, used only in the experiments with acetone, in 1:1 molar ratio.

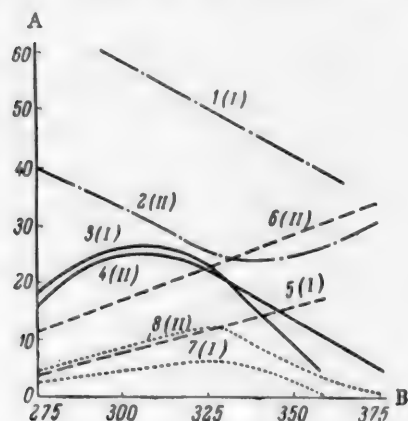


Fig. 1. Effect of temperature on ketone yields in the catalytic conversion of acetone (I) and isopropyl alcohol (II). A) Yield, wt. % on the original substance, B) temperature (°C). Yields of: 1 (I) and 2 (II) acetone; 3 (I) and 4 (II) methyl isobutyl ketone; 5 (I) and 6 (II) water; 7 (I) and 8 (II) diisobutyl ketone.

In the case of isopropyl alcohol, the latter is completely dehydrogenated to acetone, which again remains in the condensate, but in much smaller amounts (40%), as in this case side reactions yielding diisobutyl ketone and other highly condensed products are intensified. The gases (Table 2) contain propylene in addition to

These substances were passed in vapor form over a precipitated copper catalyst promoted with thorium oxide, which was found to be highly active in the production of higher ketones from ethyl alcohol [8-10].

**Effect of temperature on the yield of methyl isobutyl ketone.** The experiments were performed at 275-350° and space velocities (SV) 60 and 170-200. It follows from the data in Table 1 and Fig. 1 that the yields of methyl isobutyl ketone, both from acetone and from isopropyl alcohol, increase with temperature up to 300°, when they reach 26%. At higher temperatures the content of this ketone in the condensate decreases owing to intensified condensation of acetone, leading to the formation of diisobutyl ketone and a high-boiling residue containing up to 80% of carbonyl compounds. The formation of diisobutyl ketone in the condensate (up to 6-12%) at 325° may be attributed to secondary condensation reactions of mesityl oxide and methyl isobutyl ketone with acetone. In the experiments with acetone and hydrogen, the condensates contain up to 60% of unreacted acetone at all temperatures.

TABLE 1

Effect of Temperature on the Catalytic Conversion of Acetone and Isopropyl Alcohol into Ketones

Temperature (°C)	Condensate yield (wt. %)	Yield (wt. % on the original substance)					Total yield of higher ketones (%)
		acetone	methyl isobutyl ketone	diisobutyl ketone	water	high-boiling residue > 170°	
Acetone and hydrogen (1 : 1), SV = 180-200							
275	95.0	66.0	18.0	2.0	4.0	3.0	20.0
300	98.0	58.0	26.0	4.0	8.0	5.0	30.0
325	96.0	48.0	23.0	6.0	10.0	9.0	29.0
350	92.0	43.0	8.0	2.0	16.0	25.0	10.0
Isopropyl alcohol, SV = 60-70							
275	96.5	40.5	16.0	4.5	13.8	7.0	20.0
300	91.0	33.0	26.0	9.0	16.5	8.0	35.5
325	91.0	25.0	21.0	12.0	20.0	10.0	33.0
350	97.5	35.0	13.0	3.0	32.0	14.0	16.0
375	86.0	31.0	5.0	1.0	32.0	17.0	6.0

hydrogen; the propylene is formed at low space velocities by dehydration of isopropyl alcohol, its content reaching 8-11% at 350-375°. The average hydrogen yield at the optimum temperatures of ketone formation is 50-65% of the theoretical. This shows that about one half of the alcohol formed by the dehydration reaction

TABLE 2

Composition of Gas in the Catalytic Conversion of Isopropyl Alcohol

Temperature (°C)	Gas yield (liters/100 g of alcohol)	Composition of gas (vol.%)				Hydrogen yield (vol.% of theoretical)
		CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	CO	H <sub>2</sub>	
275	25.0	0.3	0.9	0.0	98.8	66.0
300	22.0	0.0	1.1	0.0	98.9	58.0
325	20.0	0.0	4.5	0.0	95.5	51.0
350	29.0	0.0	8.8	0.0	91.2	71.0
375	29.0	0.8	10.7	0.0	88.5	69.0

is utilized in ketone formation. Above 325° the hydrogen yield increases, with a simultaneous increase of the amount of water in the condensate (from 20 to 32%), and a sharp decrease of the methyl isobutyl ketone and diisobutyl ketone contents. This indicates a change in the direction of the acetone condensation reactions.

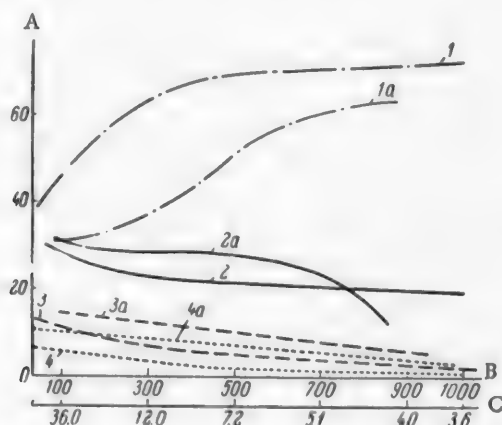


Fig. 2. Effect of space velocity on acetone conversion. A) Yield (wt.% on the original acetone), B) space velocity, C) contact time (seconds). Yields at 300 and 325° respectively: 1 and 1a) acetone; 2 and 2a) methyl isobutyl ketone; 3 and 3a) water; 4 and 4a) diisobutyl ketone.

Effect of space velocity on the yield of methyl isobutyl ketone. Table 3 and Fig. 2 give the results of experiments on the formation of methyl isobutyl ketone at different space velocities, at 300 and 325°, with 1:1 ratio (by volume) of hydrogen to acetone. The data in the table show that when the space velocity is increased from 70 to 1000 (with a 14-fold decrease of the contact time) at 300°, the yield of methyl isobutyl ketone falls by about 13%, calculated on the original acetone, because of the decreased effect of the side reactions, but increases from 60 to 75% when calculated on the converted acetone. Thus, increase of space velocity makes it possible to obtain a 15- to 17-fold increase of the output rate of the equipment.

As was noted earlier, above 300° there is an intensification of side reactions which lead to the formation of diisobutyl ketone and other high-molecular condensation products. The yield of methyl isobutyl ketone at



TABLE 3

Effect of Space Velocity on the Yields of Ketones from Acetone and Hydrogen (1:1) at 300 and 325°

SV	Contact time (seconds)	Condensate yield (wt. %)	Yields (wt. % on the original acetone)					Yield of methyl isobutyl ketone (% of theoretical on the converted acetone)
			acetone	methyl isobutyl ketone	diisobutyl ketone	water	residue > 170°	
At 300°								
70	51.5	95.0	41.0	30.0	6.0	12.0	7.0	58.0
175	20.5	94.0	54.0	24.5	5.0	6.5	5.0	63.0
300	12.0	96.0	65.0	23.0	3.0	4.2	3.0	76.0
460	8.0	97.0	62.0	22.0	2.0	6.0	3.0	67.0
1000	3.6	96.0	71.0	20.0	2.0	3.0	2.5	77.0
At 325°								
165	22.0	96.0	32.0	29.0	10.0	14.5	10.0	50.0
380	9.4	95.0	36.0	28.5	8.0	13.5	8.5	52.0
550	6.5	98.0	56.0	28.0	3.0	5.2	3.0	74.0
775	4.6	95.0	62.0	16.0	4.0	7.0	7.0	57.0

325° and space velocity 300-500 is fairly high when calculated on the reacted acetone, but the conversion of acetone into methyl isobutyl ketone is less than at 300°.

It follows from Table 4 and Fig. 3 that isopropyl alcohol is completely converted into ketones, and the yield of methyl isobutyl ketone changes little with increase of space velocity, but the degree of conversion of the alcohol into this ketone is lower than that of acetone, owing to by-product formation. Increase of temperature from 300 to 325° does not influence the yield of methyl isobutyl ketone. The gas contains up to 98-99% of hydrogen, the average yield of which is 60-70% of the theoretical.

TABLE 4

Effect of Space Velocity on the Yield of Ketones from Isopropyl Alcohol at 300 and 325°

SV	Conden- sate yield (%)	Yield of hydrogen (vol. % of theo- retical)	Yields (% on the original alcohol)					Yield of methyl isobutyl ketone (% of the theoretical on the converted alcohol)
			ace- tone	methyl isobutyl ketone	diiso- butyl ketone	water	residue >170°	
At 300°								
60	91.0	58.0	33.0	26.0	9.0	16.0	8.0	47.0
120	90.0	47.0	39.0	21.0	6.0	15.0	9.0	41.0
210	91.0	60.0	40.0	22.0	6.0	13.0	5.0	44.0
360	95.0	70.0	49.0	20.0	5.0	6.0	6.0	47.0
At 325°								
60	91.0	51.0	25.0	21.0	12.0	20.0	10.0	34.0
120	98.0	65.0	34.5	25.0	10.0	21.5	13.0	46.0
210	99.0	80.0	57.5	22.5	5.0	10.0	6.0	64.0
310	99.0	60.0	61.0	19.0	1.0	6.0	4.0	59.0

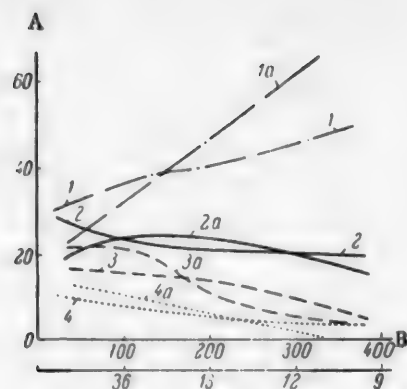


Fig. 3. Effect of space velocity on the conversion of isopropyl alcohol. A) Yield (wt. % on the original alcohol), B) space velocity, C) contact time (seconds). Yields at 300 and 325° respectively: 1 and 1a) acetone; 2 and 2a) methyl isobutyl ketone, 3 and 3a) water, 4 and 4a) diisobutyl ketone.

Conversion of mixtures of isopropyl alcohol and acetone into ketones. Since considerable amounts of hydrogen are liberated in the conversion of isopropyl alcohol into methyl isobutyl ketone, this alcohol mixed with acetone can serve as a source of hydrogen which is necessary for the formation of this ketone from acetone. Experiments were therefore carried out with mixtures of isopropyl alcohol and acetone in various proportions (Table 5). It was found that at 300° a decrease of the isopropyl alcohol content of the mixture to 30% has almost no effect on the yield of methyl isobutyl ketone, but further decrease results in a sharp fall of the ketone yield in the reaction mixture owing to hydrogen deficiency. The amount of unreacted acetone in the condensate increases, but in this case the yield of methyl isobutyl ketone, calculated on the converted substances, is considerably higher than the yield from isopropyl alcohol.

TABLE 5

Conversion of Acetone-Isopropyl Alcohol Mixtures at 300° and SV = 150

Isopropyl alcohol-acetone ratio in mixture	Condensate yield (wt.%)		Yield of hydrogen (vol. % of theoretical)	Yields (wt. % on the original mixture)				Yield of methyl isobutyl ketone (% of theoretical on the converted mixture)
	total	Including H <sub>2</sub> O		acetone	methyl isobutyl ketone	diisobutyl ketone	residue > 170°	
2 : 1	94.0	18.4	50.0	40.0	24.0	5.0	4.0	48.0
1 : 1	99.0	8.5	50.0	60.0	26.0	6.4	1.0	77.0
1 : 2	100.0	8.3	38.0	62.0	22.0	5.0	2.0	70.0
1 : 3	100.0	8.0	46.0	82.0	13.0	0.0	5.0	77.0

TABLE 6

Effect of Water Content in Isopropyl Alcohol on Ketone Yields at 300 and 325°

H <sub>2</sub> O content (wt.%)	Condensate yield (wt.%)		Yield of hydrogen (vol.% of theoretical)	Yields (wt. % on the original alcohol •)				Yield of methyl isobutyl ketone (% of theoretical on the converted alcohol)
	total	H <sub>2</sub> O		acetone	methyl-isobutyl ketone	diisobutyl ketone	residue 170°	
At 300°, SV = 220								
1.4	97.0	20.0	63.0	48.0	20.0	6.0	8.0	48.0
6.0	98.0	19.5	76.0	60.0	18.0	2.0	8.0	57.0
13.0	99.0	20.0	82.0	68.0	17.0	0.0	7.0	65.0
21.0	97.0	22.0	84.0	73.0	14.0	0.0	4.0	65.0
At 325°, SV = 150								
1.4	97.5	22.0	64.0	37.0	22.0	8.0	10.0	42.0
6.0	95.0	21.0	76.0	59.0	15.0	5.0	10.0	45.0
13.0	95.0	21.0	88.0	71.0	10.0	0.0	4.0	44.0
21.0	99.0	28.0	96.0	77.0	8.0	0.0	4.0	47.0

TABLE 7

Physicochemical Constants of the Compounds Isolated

Ketone	Boiling point (°C)		$n_D^{20}$		$d_4^{20}$		Melting point of semicarbazone derivative (°C)		Nitrogen content of semicarbazone (wt. %)	
	found	literature data*	found	literature data*	found	literature data*	found	literature data*	found	calcu- lated
Acetone ••	56.0	56.0	1.3615	1.3590	0.791	0.7912	188.5	190.0	—	—
Methyl isobutyl ketone	117.0	116.8	1.3973 <sup>17</sup>	1.3969 <sup>17</sup>	0.800	0.800	132.9	132.0	26.8	26.7
Diisobutyl ketone	168.7	168.0	1.4155 <sup>25</sup>	1.4173 <sup>25</sup>	0.806 <sup>20</sup>	0.8089 <sup>20</sup>	121—122	121.0	20.6	21.1

\* Literature reference [14]

•• Acetone obtained in the experiments with isopropyl alcohol.

Effect of water content in the alcohol on the yield of methyl isobutyl ketone. To determine the influence of water on the conversion of isopropyl alcohol into ketones, experiments were performed with different amounts of water added to the alcohol. It is known that isopropyl alcohol and water form an azeotropic mixture of b.p. 80.37° [14], containing 87.9% of the alcohol. It was dehydrated by means of solid alkali [15].

The results of experiments with alcohol containing from 1.4 to 21 wt. % of water are given in Table 6. It should be noted that an azeotropic mixture of the alcohol and water can be used for the synthesis without previous drying. With increase of the water content, the yield of methyl isobutyl ketone and other higher ketones at 300 and 325° decreases, as under these conditions water has an adverse effect on the condensation reactions of acetone. Isopropyl alcohol is completely dehydrogenated in all cases, and the gas contains 98-100% hydrogen the yield of which increases with increasing moisture content in the alcohol.

Some physicochemical characteristics of the ketones isolated in studies of the catalytic conversion of isopropyl alcohol and acetone with hydrogen are given in Table 7.

The condensate residues boiling above 170° were found to contain up to 80% of higher ketones. The presence of unsaturated compounds indicates the probable presence of isophorone in the condensates, but it is also possible that ketones formed by the condensation of methyl isobutyl ketone may be present.

Studies of the catalytic vapor-phase condensation of acetone and other methyl ketones are continuing.

## SUMMARY

1. Acetone-hydrogen mixtures, or isopropyl alcohol, can be converted into methyl isobutyl and diisobutyl ketones in presence of promoted copper catalyst.

2. The optimum conditions for the production of methyl isobutyl ketone from acetone and hydrogen are a temperature of 300° and a space velocity from 500 to 1000. Under these conditions the ketone yield is 20-22% on the weight of condensate, or 65-70% on the converted acetone, per pass.

3. The formation of methyl isobutyl ketone is accompanied by the formation of diisobutyl ketone and other higher ketones; their yield reaches 10-15% on the acetone passed.

4. The unreacted acetone can be recycled, mixed with hydrogen (1:1), or with isopropyl alcohol (2:1).

5. The maximum permissible water content in isopropyl alcohol is 13%, as the yield of methyl isobutyl ketone falls on further increase of the water content.

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## THE PEROXIDES OF VINYLACETYLENE

I. M. Dolgopol'skii and Z. F. Dobler

It is known that peroxides may be formed when molecular oxygen reacts with various organic compounds.

Unstable compounds containing considerable excess energy are formed in the course of autoxidation. These compounds readily decompose with liberation of active oxygen, which participates in further oxidation of the original substance. These concepts are based on the peroxide theory of oxidation, formulated by Bakh [1] and simultaneously by Engler [2].

Peroxide decomposition may be induced by the action of heat, and a characteristic property of unsaturated hydroperoxide is the ability to polymerize when heated. The peroxide group may be either destroyed or retained during polymerization [3]. Peroxides of alkylidene structure are unstable, and decompose explosively under impact or friction.

Investigations of the mechanism of autoxidation showed that these reactions are chain processes [4-6].

In the case of unsaturated compounds, the oxidation rate remains constant, after a short induction period, almost to the end of the reaction. Kistjakowsky [7] found that the oxidation rate of acetylene increases with increase of the oxygen concentration. The general nature of oxidation, polymerization, and thermal decomposition, regarded as chain processes involving the formation of free radicals, was determined by the work of Medvedev and his associates [8].

The structure of vinylacetylene indicates that this compound should also tend to undergo autoxidation at moderate temperatures [9].

The reported explosions in experiments with vinylacetylene polymers should probably be attributed to decomposition of peroxide compounds of vinylacetylene, or their polymers.

The aim of the present investigation was to study the conditions for the formation of vinylacetylene peroxides, and to develop methods for the prevention of autoxidation of vinylacetylene, and hence of the formation of explosive peroxides and their polymers. The effects of a number of admixtures present in vinylacetylene during oxidation, and its tendency to oxidation in chlorobenzene solution, were also studied.

In the light of available data on the inhibition of oxidation processes in unsaturated compounds [10], the possible use of phenyl- $\beta$ -naphthylamine (Neozone D) and wood-tar antioxidant (AO) for the prevention of vinylacetylene oxidation was studied.

## EXPERIMENTAL

The conditions for vinylacetylene peroxide formation were studied in experiments on the oxidation of vinylacetylene by molecular oxygen at 20°. Pure vinylacetylene was used; carbonyl compounds were previously removed from it by the action of 2% solution of hydroxylamine hydrochloride. The purified vinylacetylene was dried over calcined  $\text{CaCl}_2$  and distilled through a column of the Podbielniak type.

Experiments on the gas-phase oxidation of vinylacetylene by molecular oxygen were performed under static conditions at 20° in eudiometers. The eudiometers were glass cylinders, 500-700 ml in capacity, each with two side tubes at the top end, with one side tube sealed to a mercury manometer. The second tube was used to introduce the vinylacetylene and the other components. The calculated quantity of vinylacetylene

was introduced by means of a comb-shaped tube with three stopcocks. A bulb containing vinylacetylene was connected to one of the stopcocks. The second stopcock was attached to a eudiometer with its manometer (before the experiment,  $K_e$  for the eudiometer, i.e., the number of ml of gas equivalent to 1 mm pressure, was determined). The third stopcock was joined to a vessel filled with vinylacetylene. The whole system was evacuated, and the residual air was displaced by repeated evaporation and condensation of vinylacetylene until a constant vacuum was attained.

In experiments of the oxidation of gaseous vinylacetylene, the eudiometers were blown through and calculated amounts of vinylacetylene and oxygen were then introduced. In studies of oxygen absorption by liquid vinylacetylene, the latter was evaporated from the bulb (5 g) into the eudiometer, the lower end of which was cooled to  $-78^\circ$ . After the required amount of oxygen had been introduced from a buret, the free eudiometer outlet was sealed off. In experiments with liquid vinylacetylene the lower end of the sealed eudiometer was placed in a thermostat in order to maintain a constant vinylacetylene vapor pressure. Manometer readings were taken at intervals. The total vapor pressure ( $O_2$  and  $C_4H_4$ ) over the liquid vinylacetylene in the eudiometer gradually decreased as the result of oxygen absorption. The vapor pressure of vinylacetylene, calculated from the formula

$$P = 7.69 \frac{1338}{T}$$

was subtracted from the total pressure recorded by the manometer.

The residual oxygen pressure was converted into its volume (ml), reduced to standard conditions. To calculate the volume occupied by the oxygen in the eudiometer from the oxygen pressure, the latter was multiplied by  $K_e$  (the equivalent, in ml, of one manometer scale division for the given eudiometer).

In experiments on the gas phase oxidation of vinylacetylene, the total gas volume, reduced to standard conditions, was calculated from the manometer pressure. It was found that the total volume of the gaseous mixture remains virtually unchanged for a long time (up to 120 days). This leads to the conclusion that vinylacetylene is not oxidized in the gas phase at room temperature. This result is in good agreement with published data [11, 12].

Studies of the liquid-phase oxidation of vinylacetylene by molecular oxygen in eudiometers showed that the total vapor pressure falls with time, owing to a decrease in the partial pressure of oxygen. In parallel experiments with liquid vinylacetylene in absence of oxygen, the volume of the gas phase remained constant when reduced to standard conditions. The amount of oxygen introduced was calculated in terms of moles per 1 mole of vinylacetylene.

The results of experiments on the liquid-phase oxidation of vinylacetylene are plotted in Figs. 1 and 2; it is seen that: 1) the oxygen content of the gas phase over the liquid vinylacetylene decreases with time, as the result of absorption by vinylacetylene; 2) the rate of absorption of oxygen by liquid vinylacetylene rises with increase of the oxygen concentration in the gaseous mixture, and is a linear function of its initial concentration in the gas phase; 3) dilution of the gaseous mixture with nitrogen (Fig. 1) decreases the rate of absorption of oxygen by liquid vinylacetylene.

It should be noted that, as oxygen absorption proceeds, the colorless liquid vinylacetylene becomes yellow, and at the end of the absorption a yellow layer forms on the bottom of the eudiometer. The products formed by oxidation were separated from unchanged vinylacetylene by distillation of the latter under vacuum. After distillation of the vinylacetylene, yellow deposits remained in the eudiometers; these were extracted (the eudiometers were cut open), and tested for explosibility, solubility in acetone, chloroform, and alcohol, and for further ability to absorb more oxygen.

An artillery impact tester (Fig. 3) [13] was used for the explosibility tests on the products formed by the oxidation of vinylacetylene. All the samples were found to explode in the machine.

The oxidation products were insoluble in alcohol. They were slowly soluble in cold acetone and cold chloroform. They were no longer explosive after evaporation of the solvent.

To determine whether the oxidation products are capable of further oxygen absorption, the eudiometers were refilled with oxygen after removal of the vinylacetylene. It was found that no oxygen absorption takes place in the course of 19 days.



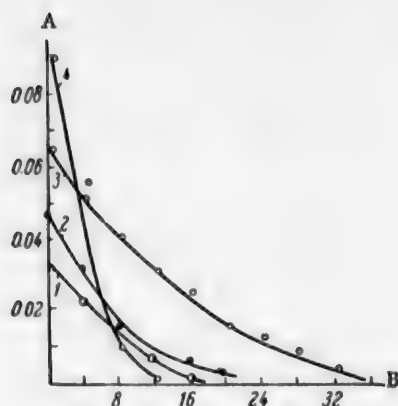


Fig. 1. Liquid-phase oxidation of vinylacetylene. A) Oxygen content of gas phase (moles  $O_2$ /mole  $C_4H_4$ ), B) oxidation time (days). Moles of oxygen introduced: 1) 0.033, 2) 0.045, 3) 0.066, 4) 0.13 mole of oxygen-nitrogen mixture.

oxidation\* of vinylacetylene in presence of these compounds.

Data on the influence of impurities on the rate of oxygen absorption are presented in Fig. 4; they indicate that in presence of 5% of chloroprene in the vinylacetylene most of the oxygen is absorbed within the first 24 hours, whereas, at the same initial oxygen concentration, pure vinylacetylene absorbs only 10% of the available oxygen during the same period.

The rate of oxygen absorption by vinylacetylene in presence of 2% water is about  $1/2$  of the rate for pure vinylacetylene.

The relationship between the absorption rate and partial pressure (concentration) of oxygen over liquid vinylacetylene in presence of chloroprene is plotted in Fig. 5. These results indicate that the oxidation rate of vinylacetylene increases 5- to 6-fold in presence of 5% chloroprene.

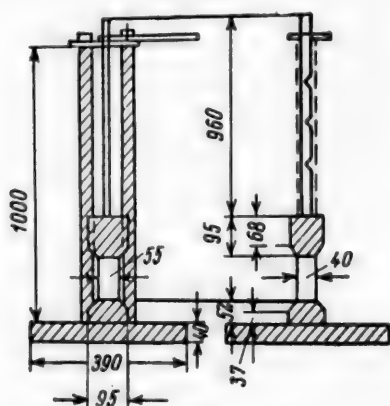


Fig. 3. Diagram of artillery impact tester.

The most suitable method for determination of active oxygen in vinylacetylene peroxides is the stannometric method of Hock and Schrader [14], modified by Ivanov [15]. The results obtained in the determinations of active oxygen in vinylacetylene after its reaction with oxygen are given in Table 1.

\* Vinylacetylene is not oxidized in the gas phase in presence of these compounds.

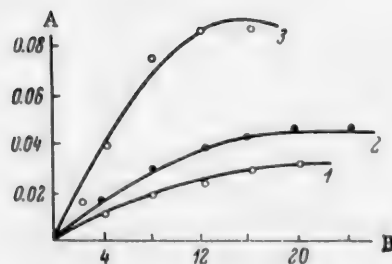


Fig. 2. Rate of liquid-phase oxidation of vinylacetylene. Amount of oxygen absorbed (moles  $O_2$ /mole  $C_4H_4$ ), B) oxidation time (days). Moles of oxygen introduced: 1) 0.033, 2) 0.045, 3) 0.090.

Effect of impurities on the rate of oxygen absorption. To determine the effects of water and acetaldehyde in the vinylacetylene, and also of chloroprene, on the rate of oxygen absorption, experiments were carried out on the liquid-phase

The oxidation products of a mixture of vinylacetylene and chloroprene, formed by the absorption of 0.16 mole of oxygen per 1 mole of vinylacetylene, are explosive. The gummy oxidation products hardened on exposure to the air, and caught fire spontaneously when removed from the glass. The oxidation products formed in vinylacetylene containing acetaldehyde and water are explosive after distillation of the vinylacetylene.

Determination of peroxides. To confirm the presence of peroxide groups in vinylacetylene after absorption of molecular oxygen, its content of active oxygen was determined.

It is known [12] that the presence of peroxides in the course of oxidation of unsaturated hydrocarbons is characterized by a number of chemical reactions which depend on the mobility of one of the oxygen atoms, known as "active" oxygen, in the peroxide group.

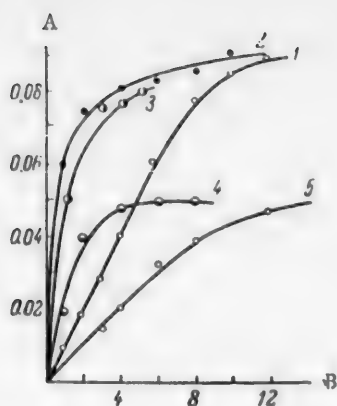


Fig. 4. Effect of oxygen on the oxidation rate of vinylacetylene in presence of impurities. A) Amount of oxygen absorbed (moles  $O_2$ /mole  $C_4H_4$ ), B) oxidation time (days). 1) 0.09 mole  $O_2$ , 2) 0.09 mole  $O_2$  + 5%  $C_4H_5Cl$ , 3) 0.08 mole  $O_2$  + 5%  $C_4H_5Cl$ , 4) 0.05 mole  $O_2$  + 5%  $C_4H_5Cl$ , 5) 0.066 mole  $O_2$  + 1%  $H_2O$ .

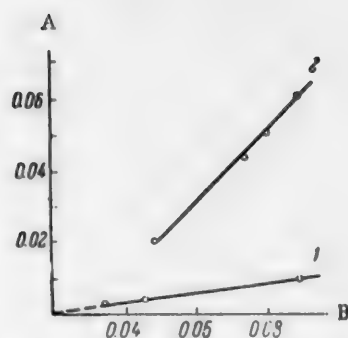


Fig. 5. Effect of initial oxygen concentration on the oxidation rate of vinylacetylene. A) Amount of oxygen absorbed (mole/24 hours), B) initial oxygen concentration (moles  $O_2$ /mole  $C_4H_4$ ). 1) Pure  $C_4H_4$ , 2)  $C_4H_4$  with an admixture of  $C_4H_5Cl$ .

TABLE 1

Determination of Active Oxygen in Vinylacetylene

Experimental conditions	Volume of 0.05 N $FeCl_3$ solution for titration		Active oxygen found (% on the $C_4H_4$ )
	control sample	with vinylacetylene	
Pure vinylacetylene immediately after distillation	8.1	8.1	Nil
Vinylacetylene 15 minutes after distillation	8.0	8.0	Nil
60 minutes after distillation	8.1	7.5	0.009
	8.0	7.4	0.009
	8.1	7.3	0.012
	8.0	7.2	0.012
5 ml of oxygen added to pure vinylacetylene, shaken for 10 minutes	7.8	7.5	0.0045
Ditto, shaken for 20 minutes	7.8	7.3	0.0075
20 ml of oxygen introduced into bulb with vinylacetylene, and left over 20 hours at $t = -70^\circ$	7.6	6.8	0.018
51 ml of oxygen introduced and left for 20 hours at $t = -70^\circ$	7.5	6.2	0.019
62 ml of oxygen introduced and left for 20 hours at $t = -70^\circ$	7.5	5.7	0.026
73 ml of oxygen introduced and left for 20 hours at $t = -70^\circ$	7.5	5.3	0.038

It is seen that no active oxygen was found in freshly-distilled vinylacetylene, whereas after contact with air a certain amount of active oxygen could be detected. The active-oxygen content increases with the amount of molecular oxygen introduced into the bulb with the liquid vinylacetylene. The presence of active oxygen in the vinylacetylene confirms that peroxides are formed as the result of oxygen absorption. Experiments on the oxidation of liquid vinylacetylene, in which the amounts of absorbed and active oxygen were determined,

TABLE 2

Determinations of Active and Absorbed Oxygen

Experiment No	Amount of oxygen (ml)		Absorption time (hours)	Oxygen absorbed (wt. % on $C_4H_6$ )	Volume (ml) of 0.1 $FeCl_3$ solution for titration		Active oxygen content (%) calculated on	
	introduced	absorbed			control sample	containing $C_4H_6$	$C_4H_6$	absorbed oxygen
1	30	25	72	0.70	10	2.4	0.13	16
2	30	26	72	0.74	20	10.1	0.15	20
3	45	41	72	1.16	30	10.0	0.31	27
4	40	18.5	24	0.54	20	7.2	0.19	38
5	40	22.8	28	0.66	20	6.6	0.22	34
6	30	15.3	18	0.44	30	18.6	0.18	42

showed that there is no linear relationship between the active oxygen content and the amount of oxygen absorbed. The oxidation was performed at 20°. The results are given in Table 2.

It follows from these results that the amount of active oxygen (as % of the amount absorbed) decreases with increase of oxidation time. In Experiment 6, when the vinylacetylene was in contact with oxygen for 18 hours, and the mixture was shaken periodically during the last 2 hours, the amount of active oxygen was 42% of the absorbed oxygen.

It follows that half the absorbed oxygen can be obtained in active form only if the contact time is reduced further.

These results indicate that the peroxides formed during the oxidation of vinylacetylene either break down gradually with liberation of active oxygen which interacts with the unoxidized vinylacetylene molecules, or are regrouped into a more stable form of lower active-oxygen content.

**Prevention of vinylacetylene oxidation.** In the light of existing literature data on the radical oxidation mechanism of saturated and unsaturated hydrocarbons it seemed likely that the autoxidation of vinylacetylene, like any chain oxidation process, could be prevented by the addition of small amounts of antioxidants. A study was therefore carried out of the absorption of oxygen by pure vinylacetylene, and by vinylacetylene containing chloroprene and iron naphthenate in presence of Neozone D (phenyl- $\beta$ -naphthylamine) and wood-tar antioxidant. The antioxidants were added before the vinylacetylene was put into the eudiometers. The subsequent experimental procedure was the same as in the determinations of oxygen absorption rate in liquid vinylacetylene without antioxidants. The vapor pressure of vinylacetylene in absence of oxygen was determined in parallel control experiments.

TABLE 3

Changes on the Volume of Oxygen over Liquid Vinylacetylene in Presence of Antioxidants

Names and amounts (%) of components added to vinylacetylene	Volume of oxygen (ml) after contact time (days)											
	0	4	8	12	16	20	24	28	32	36	40	48
1 AO*	77	77	73	72	78	72	71	75	75	75	75	75
0.6 AO	190	190	185	186	184	185	—	186	—	—	—	—
0.5 AO	85	85	84	86	82	85	—	87	—	84	—	—
0.5 Neozone D	84	84	86	81	84	85	86	86	—	—	83	—
Fe naphthenate + 0.6 AO	183	174	176	174	177	182	—	177	—	—	—	—
5 chloroprene + 1 AO	184	176	181	177	—	176	—	—	—	—	—	—
5 chloroprene + 0.6 AO	163	165	152	—	154	—	155	—	—	—	—	—
0.5 chloroprene + 0.5 AO	151	149	139	—	139	—	140	—	—	—	—	143

\* AO is wood tar antioxidant.

In absence of oxygen, vinylacetylene was unchanged for 85 days, and the residue after distillation comprised 0.5% of the original vinylacetylene by weight. The vapor pressure of vinylacetylene was within  $\pm 0.1\%$  of the theoretical (Table 3).

The results show that in presence of antioxidants liquid vinylacetylene does not absorb oxygen, and is therefore not oxidized. Absence of oxidation products was confirmed by the fact that the weights of the residues after evaporation of the vinylacetylene corresponded to the amounts of added antioxidants, and these residues did not explode when tested on the impact tester.

Simultaneously with the experiments on the oxidation of vinylacetylene, the absorption of molecular oxygen by chloroprene with and without antioxidants was investigated (Table 4).

TABLE 4  
Oxidation of Chloroprene

Components	Volume of oxygen (ml) after contact time (hours)							
	0	15	30	45	60	75	90	120
Chloroprene (4 g) . . . . .	270	166	116	85	55	—	—	25
Chloroprene (4.5 g) . . . . .	250	196	74	54	—	24	0	—
Chloroprene (4 g) + 0.5% AO . . . . .	285	285	285	282	280	—	—	275
Chloroprene (4.5 g) + 0.59% AO . . . . .	287	287	287	288	288	—	—	288

It is seen that chloroprene absorbs oxygen at a much higher rate than does vinylacetylene. In absence of antioxidant the chloroprene gradually turned yellow on contact with oxygen, and finally became dark brown. The rubberlike residue after distillation of the chloroprene had a sharp odor of chloroprene dimers. In presence of wood tar antioxidant (AO) chloroprene was neither polymerized nor oxidized.

Oxidation of vinylacetylene in chlorobenzene solution was studied in eudiometers. It was first shown that pure chlorobenzene does not absorb oxygen. The vinylacetylene concentration of the solution was varied from 2 to 50% (Table 5).

TABLE 5  
Absorption of Oxygen by Solutions of Vinylacetylene in Chlorobenzene

Concentration of vinylacetylene in chlorobenzene (%)	Oxygen introduced (ml)	Residual oxygen (ml) after contact time (hours)			Total oxygen absorbed (ml)
		24	93	240	
50	100	87	41	—	59
30	100	96	92	—	8
10	100	100	100	94	6
2	100	100	100	100	0

It follows from these results that there is no appreciable absorption of oxygen during 10 days in a solution containing 2% vinylacetylene.

At higher concentrations of vinylacetylene (10–50%) oxygen is absorbed, the absorption rate increasing with the vinylacetylene concentration. Determinations of active oxygen showed that peroxide compounds are formed. For example, a 50% solution of vinylacetylene in chlorobenzene after 4 days contained 0.012 g of active oxygen, i.e., 16.6% of the amount absorbed. A 30% solution (after 4 days) contained 0.0048 g of active

oxygen, or about 40% of the oxygen absorbed. Oxygen was not absorbed (during the same contact time) after the addition of 1% wood tar antioxidant to 50% vinylacetylene solution.

It follows that when vinylacetylene solutions are brought into contact with molecular oxygen in absence of antioxidants the vinylacetylene is oxidized, although slowly.

#### SUMMARY

1. Gaseous vinylacetylene is not oxidized by molecular oxygen at room temperature (20°).
2. Liquid vinylacetylene absorbs molecular oxygen with the formation of explosive peroxides.
3. The oxidation of vinylacetylene, and therefore the formation of explosive products, can be prevented by the addition of antioxidants.
4. The oxidation rate of vinylacetylene is increased considerably in presence of chloroprene.
5. The absorption of oxygen by vinylacetylene in chlorobenzene solution was studied, and the influence of dilution of vinylacetylene by a solvent on its oxidation rate was demonstrated.

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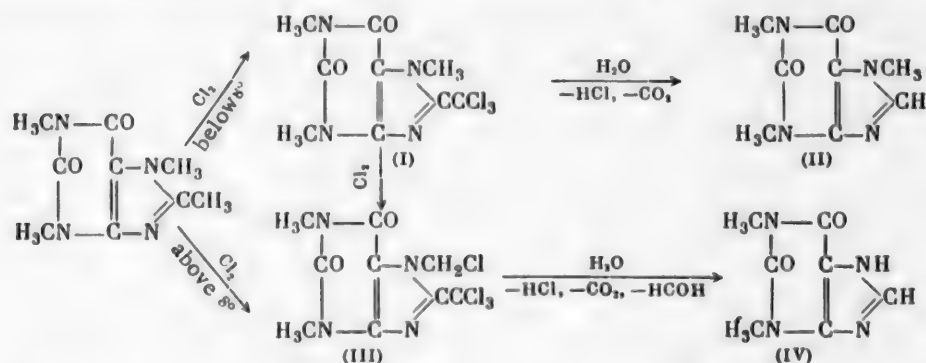
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\*In Russian.

# THE REACTION OF FORMATION OF 8-TRICHLOROMETHYLCAFFEINE •

E. S. Golovchinskaya

In the method developed earlier by the present author [1] for the production of 8-trichloromethylcaffeine (I), an intermediate in the synthesis of caffeine (II), an excess of chlorine acts on a suspension of methylcaffeine in dry chlorobenzene on cooling. It was then found that the reaction temperature must not exceed 8°, because at higher temperatures chlorine may replace hydrogen in the methyl group in the 7 position, with formation of 8-trichloromethyl-7-chloromethyltheophylline (III), an intermediate in the synthesis of theophylline (IV).



On the other hand, it was found that the formation of (I) at low temperatures requires the use of not less than 6 moles of chlorine, i.e., 200% of the calculated quantity. •• If less excess chlorine is used, normal completion of the reaction is prevented even if the chlorination is performed without cooling, at room temperature.

A more detailed study of the chlorination of methylcaffeine revealed the following peculiarity, which required a full explanation.

Attempts to bring about the reaction with 4.5 or 5 moles of chlorine instead of 6, i.e., with 150-183% of the theoretical quantity, yielded a thick reaction mass consisting of a complex mixture of chlorinated substances. A considerable amount of "free" chlorine could be found in it by titration. It was observed that the amount of titratable chlorine remained constant, not only if the reaction mass was stirred for a long time or if a fresh portion of methylcaffeine was added, but also if air was blown through it. However, as soon as 1-1.5 moles of chlorine, i.e., the amount required to make up the deficiency below 6 moles, was added to the underchlorinated mass, the substance dissolved to give a transparent solution, and most of the excess chlorine again became capable of reacting with methylcaffeine or its 8-mono- and dichloro derivatives [2], and could also be rapidly removed from the solution by a current of dry air.

These observations gave rise to the suggestion that the intermediate substances formed in the preparation of (I) from methylcaffeine (namely, 8-monochloro- or 8-dichloromethylcaffeine, or both) are capable of forming

• Communication III in the series on the synthesis of purine alkaloids from uric acid.

•• All the excess chlorine is absorbed almost completely by the reaction mass. At the end of the reaction it can be quantitatively titrated with thiosulfate in a sample of the solution in KI solution, whereas iodine is not liberated in receivers containing KI solution placed at the exit from the apparatus.

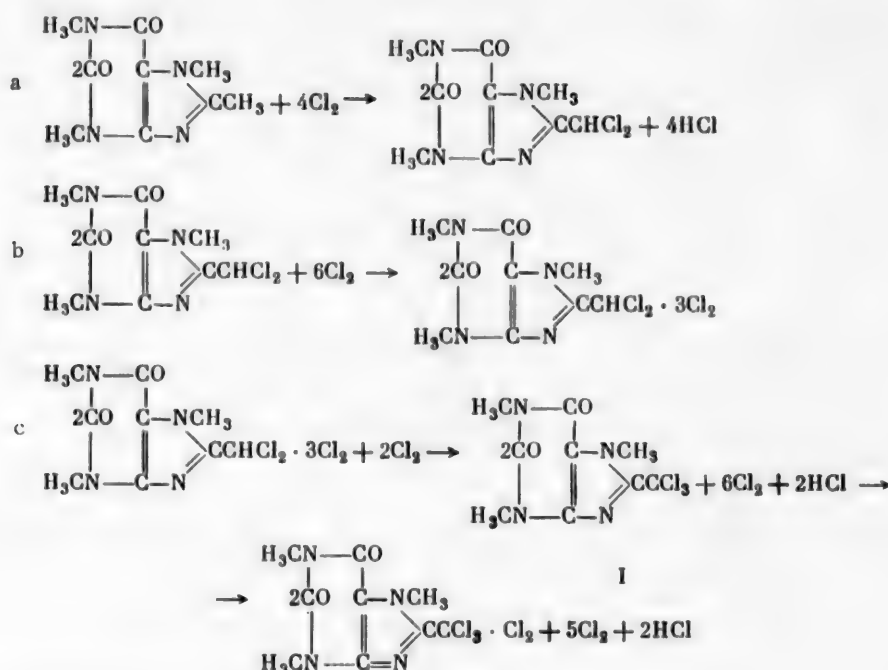


addition compounds with chlorine. The fact that the chlorine in such compounds, which naturally loses its ability to replace hydrogen under the ordinary reaction conditions, can nevertheless displace iodine from aqueous KI solutions, can be easily explained by the instability of the addition products in water, and their decomposition during titration with aqueous KI solution. The original methylcaffeine evidently does not form addition compounds with chlorine, as shown by the fact that, as soon as it comes in contact with chlorine, HCl is liberated and heat is evolved.

It was further found that at the end of the reaction not all the excess chlorine which could be titrated with thiosulfate (i.e., not all 3 moles) could be removed from the chlorinated solution in an air stream, or combined with a fresh portion of methylcaffeine. The reaction solution, i.e., the solution of (I) in chlorobenzene, invariably retained a small amount of chlorine\*, about 0.5 mole, which could be titrated with thiosulfate, but did not react even with unsaturated hydrocarbons. These experiments showed that (I) is also capable of combining with a certain amount of chlorine to give an addition compound which is readily decomposed during titration; this was confirmed by experiments in which solutions of pure (I) in other organic solvents were saturated with chlorine.

The formation of similar addition compounds in the purine series has recently been reported. In 1956, Brederick et al. [3] described the addition compounds of bromine with purine hydrobromide and with free purine. These addition compounds (especially the compound without HBr) are easily decomposed by water and break down rapidly on increase of temperature.

The explanation of the peculiarities found in the chlorination process should probably be sought in the ability of the intermediate 8-chloro derivatives of methylcaffeine to add on more chlorine than (I). For example, the conversion of methylcaffeine into (I) might be represented as follows:



An analogous mechanism might be postulated for 8-monochloromethylcaffeine.

To isolate (I) from the reaction solution after removal of the liberated excess chlorine, the chlorobenzene is distilled off under vacuum and the crystalline residue is washed with a small amount of alcohol. If the chlorobenzene is distilled off at temperature not exceeding 60-70°, the substance obtained after the alcohol treatment

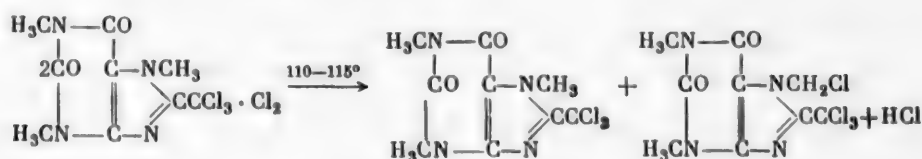
\* A control experiment, in which pure chlorobenzene was saturated with chlorine and hydrogen chloride, confirmed that both gases are blown out from the solution quantitatively in a current of air, and can be titrated in receivers.

is fairly pure (I), of m.p. 180-182°. The yield is about 90% of the theoretical, and small amounts of (III) can be detected analytically in it only in rare instances. "Residual" chlorine can never be detected either in the chlorobenzene distillate, or in the wash bottles with KI solution placed between the pump and receiver. The chlorine is retained by the crystalline residue after distillation of the chlorobenzene, and then enters the alcoholic mother liquor (probably as the result of decomposition of the unstable addition compound by alcohol). It can be titrated in the residue after distillation of the solvent, before alcohol treatment.

However, further experiments showed that if the chlorobenzene is distilled off at a higher temperature (above 100°), the (I) formed always contains a considerable admixture of (III) (25-30%), probably formed by chlorination of (I) by "residual" chlorine.

This observation was confirmed by numerous experiments. Methylcaffeine was chlorinated under standard conditions (in chlorobenzene, temperature below 8°, 6 moles of chlorine). All the free chlorine dissolved in the reaction mixture was blown out by means of air or combined with methylcaffeine, and the bound chlorine remaining in solution was determined by titration of a sample with thiosulfate in KI solution. The solution was then divided into portions, chlorobenzene was distilled off at different temperatures from these portions, the reaction product was washed with alcohol, and (III) was determined quantitatively in the products. •

The experiments showed convincingly that at 60-70° the chlorine bound with (I) by labile bonds cannot take part in the chlorination reaction; at higher temperatures, this chlorine is liberated and replaces hydrogen in the methyl group in position 7. Breakdown of the presumed addition compound (I. Cl<sub>2</sub>) on heating, and its conversion into (III), may be represented as follows:



These results are in agreement with the observations of Bredereck et al. [3], and indicate the thermal instability of the halogen-addition compounds of the purine series. They formed the basis of attempts to prepare (I) by the reaction of methylcaffeine with 3 moles of chlorine without the use of excess chlorine, a necessary condition being that the reaction be carried out above the decomposition temperature of the addition compounds, i.e., under conditions such that the latter are unlikely to exist.

Success in this task depended on the sequence in which the methyl-group hydrogens in the 7 and 8 positions of the methylcaffeine molecule are replaced by chlorine at high temperatures. This question was investigated by studies of reactions of mixtures of (I) with methylcaffeine, and of a three-component mixture of (I), methylcaffeine, and 8-dichloromethylcaffeine, with chlorine at 110-115°. The amount of chlorine in these reactions did not exceed the amount necessary for the conversion of all the methylcaffeine and dichloromethylcaffeine into (I). In all cases the reaction products were found to consist either of pure (I) or (if there was insufficient chlorine) of a mixture of (I) with dichloromethylcaffeine. No appreciable amounts of the tetrachloro derivative (III) were found in any of the products, whereas its formation would be inevitable if the chlorination of (I) took place first, or if chlorination of both components in the mixtures proceeded simultaneously. These experiments proved that even at high temperatures the methyl hydrogens in the 7 position are not replaced by chlorine until the reaction mass contains compounds capable of chlorine substitution in the 8 position, namely: methylcaffeine, 8-monochloro-, and 8-dichloromethylcaffeine. They therefore demonstrated clearly that if the amount of chlorine taken for the reaction does not exceed 3 moles per mole of methylcaffeine, (I) can be prepared at a high temperature without the risk that the 7-chloromethyl-8-trichloromethyl derivative would be formed as an impurity.

These results were used in the development of an improved method, described below, for the preparation of (I). This method has a number of important practical advantages over the earlier method. Since the reaction

• The author offers her deep gratitude to A. N. Kurteva, N. S. Goriacheva, and A. K. Ruzhentseva for assistance in this work.

is performed without cooling, the chlorination process is accelerated considerably, because in order to maintain a low temperature in the exothermic reaction of methylcaffeine chlorination the chlorine must be supplied slowly, with intensive cooling. Moreover, the absence of excess chlorine eliminates the very laborious removal of large amounts of free chlorine from the reaction solution after the end of chlorination – an operation which requires special equipment when performed on the large scale. Finally, the treatment of the reaction mass is simplified because it is possible to distill off the solvent at any desired temperature without the danger that part of the (I) may be converted into the tetrachloro derivative (II).

Investigations of the addition products of chlorine and 8-mono, di-, and trichloromethylcaffeine, for a more detailed characterization of these unstable substances, are continuing. •

## EXPERIMENTAL

Preparation of the addition compound of chlorine and 8-trichloromethylcaffeine (I). 1) Dry chlorine was passed into a solution of 5 g of (I) in 50 ml of dry chloroform at 5° until the weight increased by 7 g. Titration of a sample of the chlorinated solution with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  in 20% KI showed a chlorine content of 0.127 g per ml. Dry air was blown through the solution for 1 hour, and the chloroform was then evaporated under vacuum at room temperature. The smeary white oily residue reddens in air, attracts moisture, and lumes. Part of the residue was treated with alcohol; the product was a white crystalline substance of m.p. 180–181°; a mixed sample with the original (I) melted at 180–181°. Another portion was treated with dry pentane and separated off by suction. The product was a white crystalline substance of m.p. 140–160°. A 0.3485 g sample in 50 ml of 20% KI solution was dissolved in freshly distilled chloroform and titrated with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . The free chlorine found was 0.0383 g, or 10.9%. 2) 1.85 g of chlorine was introduced into a solution of 5 g of (I) in 50 ml of dry chloroform, and dry air was blown through for 3.5 hours. The chlorine found by titration in receivers with KI solution was 1.205 g (and not 1.27 g). No more iodine was liberated from the KI solution when more air was blown through. Chloroform was evaporated off under vacuum without heat, and the residue was treated with alcohol. The yield was 4.85 g, or 97% of the theoretical, m.p. 181–182°. 3) Dry air was blown through a solution of 5 g of (I) in 50 ml of dry benzene, saturated with 5.06 g of dry chlorine, the benzene was driven off under vacuum (water bath temperature not over 35°); the residue – a glassy mass which fumed in air – was dissolved in chloroform, treated with KI solution, and titrated with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . The chlorine content was 0.48 g, or 9.6%. 4) 50 ml of dry chlorobenzene was saturated with hydrogen chloride in the cold, and then with chlorine. 1 ml of the solution was found to contain, by analysis, 0.004745 g HCl (titration with 0.1 N NaOH) and 0.038 g chlorine (by 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ ). The volume of the solution was 47.5 ml, i.e., the total HCl in the solution was 0.225 g, and the total chlorine was 1.8 g. Dry air was blown through for 30 minutes. The receivers contained 0.2164 g HCl and 1.7377 g chlorine, i.e., 96.2 and 96.5% of the amounts taken. No traces of HCl or Cl were detected in the blown chlorobenzene.

Reaction of a mixture of (I) and methylcaffeine with chlorine. 1) Hydrogen chloride, followed by chlorine, was passed into 120 ml of dry chlorobenzene at room temperature. The solution contained, by analysis, 0.64 g HCl and 13.2 g chlorine. A mixture of 5.25 g of (I) of m.p. 181.5–182°, and 13.5 g of methylcaffeine was added to it, with stirring. The suspension was rapidly heated to 110–115° and held at this temperature of 1 hour. The chlorobenzene was evaporated off, and the residue was washed with alcohol and dried. The m.p. of the (I) so obtained was 180–182°; the substance contained, by analysis, 98.3% of (I) and 0.5% of 8-dichloromethylcaffeine; the weight was 22.7 g, or 87.8% of the theoretical yield of (I). 2) Chlorine was passed through 100 ml of dry chlorobenzene. The resultant solution contained, by analysis, 9.5 g of chlorine. 6.5 g of methylcaffeine was rapidly added, the reaction mixture was heated to 110°, and stirred at 110–115° for 1 hour. The chlorobenzene was distilled off under vacuum, and the residue was treated with alcohol, separated off by suction, and dried. The m.p. of the (I) obtained was 181–182°, and analysis showed absence of (III); the weight was 18.47 g, or 88% of the theoretical quantity.

Reaction of a mixture of (I), methylcaffeine, and dichloromethylcaffeine with chlorine. Chlorine was introduced into 150 ml of dry chlorobenzene. The solution contained, by analysis, 7.85 g of chlorine. 7 g of (I) was added with stirring, the mixture was cooled to 5°, 5 g of methylcaffeine and 11.2 g of 8-(dichloro-

• The author thanks Prof. O.Iu. Magidson for his kind help in the present investigation.

methylcaffeine were added, the mixture was heated to 110-115°, kept at that temperature for one hour, the chlorobenzene was driven off, the residue was treated with alcohol, and (I) of m.p. 180.5-182° was isolated; analysis showed it to be free from (III) and 8-(dichloromethyl)caffeine. The weight of (I) was 23.5 g, or 86.9% of the theoretical quantity.

**Preparation of 8-trichloromethylcaffeine I** 43 g of chlorine, prepared from  $\text{KMnO}_4$  and  $\text{HCl}$  (sp. gr. 1.17) and dried over  $\text{H}_2\text{SO}_4$ , was introduced, with stirring, into a mixture of 20.8 g of thoroughly dried methylcaffeine and 120 ml of dry chlorobenzene. The reaction temperature was 5-7°, time 1 hour 45 minutes. At the end of the chlorine addition all the substances dissolved and the reaction mass became clear. Titration of a sample of solution in KI solution with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  showed it to contain 19.1 g of chlorine (0.127 g of chlorine in 1 ml of solution, total volume 150 ml). No iodine was liberated in wash bottles containing KI solution placed at the exit. Dry air was blown through the solution for 2 hours at 5-7°; subsequent titration of a sample showed the solution to contain 3.27 g of chlorine (0.0266 g in 1 ml, total volume 123 ml). The solution was divided into two equal parts. From one part, chlorobenzene was slowly evaporated off under a moderate vacuum at 110-115° (vapor temperature). The residue, a substance resembling caramel, crystallized when treated with 5 ml of alcohol; the crystals were filtered out, washed with alcohol, and dried at 90°; the weight was 14.6 g, m.p. 165-174°. The substance contained, by analysis, 69.7% of (I) (i.e., 10.18 g of (I), or 65.3% of the theoretical yield). It was boiled with 70 ml of water for 7 hours under reflux until completely dissolved; a sharp odor of formaldehyde was noted. The cooled acid solution was neutralized by 20%  $\text{NaOH}$ ; more alkali was then cautiously added to the thick mass with vigorous stirring in the cold, to pH 9-10 (thymolphthalein indicator); the precipitate was filtered off, and thoroughly washed with cold water. The weight of the dried caffeine was 4.9 g, or 77% of the theoretical yield calculated on (I); m.p. 228-232°. The filtrate was acidified with hydrochloric acid (1:1) to isolate theophylline; the weight obtained was 1.35 g, i.e. 75% calculated on (III); m.p. 267°.

Chlorobenzene was evaporated from the second part of the solution under vacuum at 60-70°. The white crystalline residue was washed with 5 ml of alcohol and dried at 50°. The weight was 13.9 g, m.p. 180-182°; analysis showed it to contain 94.5% of (I), i.e., 13.2 g, or 84.7% of the theoretical yield; the content of (III) was 0.48%. The substance was boiled with 70 ml of water until completely dissolved (3 hours), carefully neutralized in the cold (to pH 6.2-6.5), and the caffeine was separated off; the yield was 7.5 g, or 91% of the theoretical, m.p. 233-234°. A faint odor of formaldehyde was noted during the hydrolysis. 2) A rapid stream of chlorine, dried over  $\text{H}_2\text{SO}_4$ , was passed from a cylinder into a stirred and cooled mixture (temperature not over 8°) of 20.8 g of methylcaffeine and 120 ml of chlorobenzene. The chlorine stream was stopped as soon as the suspended substance dissolved completely and a clear solution was formed. At this instant copious evolution of iodine commenced in the wash bottles containing KI solution (which remained colorless until the end of the reaction) placed at the exit. Reaction time was 45 minutes. Dry air was blown through the chlorinated solution at 5-7° for 3 hours (until iodine evolution ceased in the KI solution in the wash bottles at the exit); the titratable chlorine content in the solution was then 3.05 g (0.0257 g in 1 ml of solution, total volume 118 ml). The solution was divided into two equal parts. One was heated under vacuum for 4 hours at 110-115° to drive off chlorobenzene, and the residue was treated with alcohol; a crystalline substance of m.p. 162-174° was obtained. The weight was 15.1 g, and it contained, by analysis, 59.7% of (I) and 31.2% of (III). The second part of the solution was heated under vacuum for 4 hours at 60-70° to drive off chlorobenzene, and then was treated with alcohol; the weight of the substance obtained was 13.3 g, m.p. 181-182°; analysis showed it to contain 96% of (I), or 12.8 g of pure (I), which is 82% of the theoretical yield; (III) was not detected. 3) 11.87 g of chlorine, prepared from 10.7 g of  $\text{KMnO}_4$  and 100 ml of  $\text{HCl}$  (sp. gr. 1.17) was passed into a mixture of 10 g of methylcaffeine and 60 ml of chlorobenzene. The chlorine was first passed through a system of wash bottles containing  $\text{H}_2\text{SO}_4$ . The process was continued for 45 minutes with stirring and without external cooling. The temperature of the mass reached 48° owing to evolution of heat during the reaction. The reaction mass was heated for 1 hour at 55-60°, and 1 hour at 110-115°; the substance dissolved completely, and the cooled reaction mixture contained 0.49 g of chlorine (0.0071 g in 1 ml of solution, volume 70 ml). The chlorobenzene was evaporated under vacuum (the temperature is immaterial), and the residue was treated with alcohol and separated off by suction. The m.p. of the reaction product was 178-179°, yield 12.3 g; it contained, by analysis, 90.6% of (I) and 8.6% of 8-(dichloromethyl)caffeine, and no (III). 0.125 g of chlorine was found by titration in the KI solution which absorbed chlorine leaving the apparatus. A further 1.295 g of chlorine was found in the apparatus for chlorine preparation and in the wash bottles with  $\text{H}_2\text{SO}_4$ . Thus, the total amount of unreacted chlorine was 0.49 g + 0.125 g + 1.295 g = 1.91 g. Therefore, 11.87 g - 1.91 g = 9.96 g of chlorine took part in the reaction.

The conversion of 10 g of methylcaffeine into (I) requires 10.24 g of chlorine. The chlorine deficiency,  $10.24 \text{ g} - 9.96 \text{ g} = 0.28 \text{ g}$ , should, by calculation, correspond to 8.21% of 8-(dichloromethyl)caffeine in the (I) obtained. 4) Chlorine, dried over  $\text{H}_2\text{SO}_4$ , was passed from a cylinder into a mixture of 20.8 g of methylcaffeine (0.1 mole) and 120 ml of chlorobenzene to a weight increase of 22.3 g (3.14 moles). The temperature of the reaction mass rose to  $47^\circ$ . It was heated for 1 hour at  $55^\circ$ , and a further hour at  $110-115^\circ$ ; the chlorobenzene was then distilled off under vacuum (the temperature is immaterial). The residue was treated with 10 ml of alcohol, separated by suction, and dried. The weight was 28.0 g, m.p.  $181-182^\circ$ ; the amount of (I) in it was 97.8%, so that the yield of pure (I) was 27.4 g or 88% of the theoretical; neither (III) nor 8-(dichloromethyl)caffeine was detected by analysis.

#### SUMMARY

1. It was found that 8-chloro derivatives of methylcaffeine, when dissolved in organic solvents, combine with a certain amount of chlorine, probably with the formation of unstable addition compounds. The bound chlorine does not take part in the ordinary chlorination reactions, but is liberated on heating or by the action of aqueous potassium iodide solution.

2. A method was found for the preparation of 8-(trichloromethyl)caffeine, based on the interaction of methylcaffeine with 3 moles of chlorine at a temperature above the temperature at which the chlorine bound by 8-chloroderivatives of methylcaffeine is liberated.

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\*In Russian.



# SOLVENT EXTRACTION OF ACETIC ACID FROM AQUEOUS SOLUTIONS

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The authors of the present paper studied the extraction of acetic acid from an aqueous phase by a non-aqueous solvent, on the assumption that the organic solvent contains no acetic acid at the entry into the extractor [1]. However, under industrial conditions the solvent entering the extractor always contains a certain amount of acetic acid. Experience shows that the acetic acid content of the solvent increases with the duration of its use. At the start of the process, when fresh solvent is introduced into the system, its acid content is at its lowest; it then increases gradually, and, according to analytical data from some plants, the acid content may reach 1.61% on untimely renewal by a fresh portion of solvent.

The gradual increase of the acidity of the solvent is caused by contamination with impurities, especially oily substances, which enter the extract from the acid liquor together with the acetic acid. Acetic acid forms complex compounds, boiling near the boiling point of the organic solvent, with the oily substances [2]. The complexes distill together with the solvent when this is distilled from the extractor. They return to the extractor together with the solvent, and thus interfere with normal extraction. This paper deals with the effect of solvent acidity on the degree of extraction of acetic acid, and with the distribution of the acidity in the aqueous phases at different levels in the extractor.

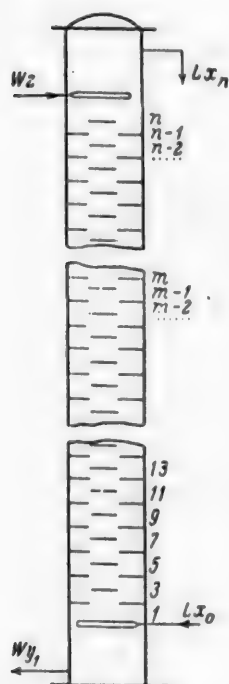


Fig. 1. Extractor.

Suppose that  $W$  liters of water containing  $z$  g of acetic acid per liter of water, and  $L$  liters of organic solvent containing  $x_0$  g of acid per liter of pure solvent, enter the extractor (Fig. 1). The acetic-acid contents in the sections 1, 2, 3, . . .  $n$  (respectively) are denoted as follows: in water,  $y_1, y_2, \dots y_n$ , in the organic solvent,  $x_1, x_2, \dots x_n$ . The sections are numbered from below. It is assumed that equilibrium distribution of acetic acid between the nonaqueous and aqueous phases is reached in each section.

The material balance for the acid in each section is as follows:

## Incoming acid.

1. The amount of acid (in g) entering the first section of the extractor with  $L$  liters of solvent is  $Lx_0$ .
2. The amount of acid (in g) flowing down from the second section to the first, with  $W$  liters of water, is  $Wy_2$ .

Total incoming acid

$$Lx_0 + Wy_2 \text{ g of acid.}$$

## Outgoing acid.

1. The amount of acid (in g) leaving the extractor with  $W$  liters of water is  $Wy_1$ .
2. The amount of acid (in g) carried over with  $L$  liters of organic solvent from the first section to the second is  $Lx_1$ .



Total outgoing acid

$$Wy_1 + Lx_1 \text{ g of acid.}$$

Since these amounts are equal, we have:

$$Lx_0 + Wy_2 = Wy_1 + Lx_1.$$

And hence

$$W(y_2 - y_1) = L(x_1 - x_0).$$

Analogously, for the second, third, etc. sections we have equations of the form

$$W(y_m - y_{m-1}) = L(x_{m-1} - x_{m-2})$$

$$m = 3, 4, \dots n.$$

Thus, we have a series of equations:

$$\left. \begin{aligned} W(y_2 - y_1) &= L(x_1 - x_0), \\ W(y_3 - y_2) &= L(x_2 - x_1), \\ &\dots \dots \dots \\ W(y_n - y_{n-1}) &= L(x_n - x_{n-1}). \end{aligned} \right\} \quad (1)$$

As for Equation (1), we find an equation for the difference between the acetic acid concentration in the feed liquor and its concentration in the aqueous phase in the last section:

$$W(z - y_n) = L(x_n - x_{n-1}). \quad (2)$$

We use the distribution coefficient

$$k = \frac{x}{y},$$

where  $x$  is the acetic acid concentration of the nonaqueous phase (in g/liter), and  $y$  is the corresponding concentration of the aqueous phase, to substitute into Equations (1), (2)

$$x_1 = ky_1, \quad x_2 = ky_2, \quad \dots \quad x_n = ky_n.$$

After such substitution, Equations (1), (2) may be written as:

$$\left. \begin{aligned} y_2 - y_1 &= \frac{kL}{W} \cdot y_1 - \frac{x_0 L}{W}, \\ y_3 - y_2 &= \frac{kL}{W} \cdot (y_2 - y_1), \\ &\dots \dots \dots \\ y_n - y_{n-1} &= \frac{kL}{W} (y_{n-1} - y_{n-2}). \end{aligned} \right\} \quad (3)$$

$$z - y_n = \frac{kL}{W} \cdot (y_n - y_{n-1}). \quad (4)$$

In Equations (3), starting with the second, we replace  $y_2 - y_1$  by its value for the first equation,  $(y_3 - y_2)$  in the third equation by its value from the second, etc., and introduce the characteristic parameters

$$(5)$$

we then have

$$P = \frac{kL}{W}, \quad R = \frac{x_0 L}{W},$$

$$\left. \begin{aligned} y_2 - y_1 &= p \cdot y_1 - R, \\ y_3 - y_2 &= p^2 \cdot y_1 - pR, \\ &\dots \dots \dots \\ y_n - y_{n-1} &= p^{n-1} \cdot y_1 - p^{n-2} \cdot R. \end{aligned} \right\} \quad (6)$$

It is assumed that in the Equations (6)

$$py_1 - R \neq 0. \quad (6a)$$

Addition of Equations (6) gives

$$y_n - y_1 = \frac{y_1 (p^n - p) - R (p^{n-1} - 1)}{p - 1}. \quad (7)$$

Consider the case when in Equation (7)  $p \neq 1$ . From Equation (7) we find

$$y_n = \frac{y_1 (p^n - 1) - R (p^{n-1} - 1)}{p - 1}. \quad (8)$$

Equation (4), after substitution of the expression from Equation (6) for  $y_n - y_{n-1}$ , takes the form:

$$z - y_n = p^n \cdot y_1 - p^{n-1} \cdot R. \quad (9)$$

Substituting into Equation (9) the expression for  $y_n$  from Equation (8), we have

$$z = \frac{y_1 (p^{n+1} - 1) - R (p^n - 1)}{p - 1}. \quad (10)$$

From Equation (10) we have

$$p^n = \frac{z(p - 1) + y_1 - R}{py_1 - R}, \quad (11)$$

where, by the Condition (6a)

$$py_1 - R \neq 0.$$

Suppose further that in Equation (11)

$$p > 1 \quad (11a)$$

In Equation (11), the numerator and denominator of the right-hand side must be both positive or both negative. We assume that in Equation (11)

$$py_1 - R > 0. \quad (12)$$

From Equation (11), we find a formula for determination of the number of extractor sections

$$n = \frac{\log[z(p - 1) + y_1 - R] - \log(py_1 - R)}{\log p}. \quad (13)$$

From (12), with Equations (5) taken into account, we have:

$$y_1 > \frac{x_0}{k}. \quad (14)$$

Equation (10) gives an expression for the concentration of acetic acid in the acid liquor leaving the extractor:

$$y_1 = \frac{z(p - 1) + R(p^n - 1)}{p^{n+1} - 1}. \quad (15)$$

Consider a continuous function of the argument  $n \geq 0$  of the form of (15) when  $p > 1$ .

It follows from Equation (15) that:

$$(y_1)_{n=0} = z, \quad \lim_{n \rightarrow +\infty} y_1 = \frac{R}{p} = \frac{x_0}{k} \quad (16)$$

To determine the course of  $y_1$ , we find from Equation (15):

$$\frac{dy_1}{dn} = \frac{(p-1)(R-pz)p^n \ln p}{(p^{n+1}-1)^2}; \quad (17)$$

$$\frac{d^2 y_1}{dn^2} = \frac{-(p-1)(R-pz)p^n(1+p^{n+1}) \ln^2 p}{(p^{n+1}-1)^3}. \quad (18)$$

First consider the case when in Equation (17)

$$R - pz \neq 0. \quad (19)$$

It follows from Equation (17) that  $y_1$  is a monotonic function. By the Inequality (14),  $y_1$  cannot be an increasing function, since in that case, in view of Equation (16), we would have

$$y_1 < \frac{x_0}{k},$$

which is contrary to (14).

Hence  $y_1$  is a monotonically decreasing function:

$$R - pz < 0, \quad (20)$$

and the graph of  $y_1$  (Equation 15), in accordance with Equation (18), when  $n \geq 0$  and  $p > 1$ , is concave (Fig. 2).

The Condition (12) or the Inequality (14) which follows from it

$$y_1 > \frac{x_0}{k}$$

indicates that acetic acid is extracted from the aqueous phase by the nonaqueous phase. In normal operation of the extractor, whatever the number of sections in it, the concentration  $y_1$  in the first section always conforms to the inequality (14).

$$y_1 > \frac{x_0}{k}.$$

The material balance for each of  $m$  sections of the extractor ( $m \leq n$ ) gives, by analogy with Equation (6)

$$\left. \begin{aligned} y_2 - y_1 &= py_1 - R, \\ y_3 - y_2 &= p^2 \cdot y_1 - pR, \\ &\dots \dots \dots \\ y_m - y_{m-1} &= p^{m-1} \cdot y_1 - p^{m-2} \cdot R \end{aligned} \right\} \quad (21)$$

Addition of Equations (21) gives

$$y_m - y_1 = \frac{y_1(p^m - p) - R(p^{m-1} - 1)}{p - 1}. \quad (22)$$

We replace  $y_1$  in Equation (22) by the expression from Equation (15)

$$y_m = \frac{z(p^m - 1) + R(p^n - p^{m-1})}{p^{n+1} - 1}. \quad (23)$$

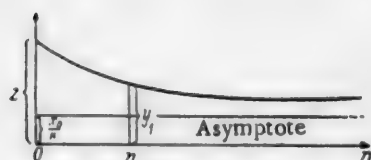


Fig. 2. Variation of the acetic acid concentration in the aqueous phase in the first section of the extractor when  $p > 1$  and  $y_1 > \frac{x_0}{k}$ .

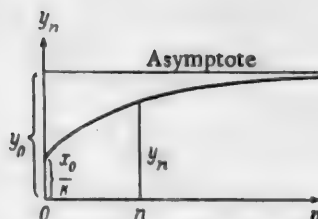


Fig. 3. Variation of the acetic acid concentration in the aqueous phase in the last section of the extractor when  $p > 1$  and  $y_1 > \frac{x_0}{k}$ .

Equation (23) can be used to calculate the acetic acid concentration in any section of the extractor, with known  $m$ ,  $n$ ,  $z$ ,  $p$ ,  $R$ .

If in Equation (23) we put  $m = n$ , we have a formula for calculation of the acetic acid concentration of the aqueous phase in the last section

$$y_n = \frac{(z + R)p^n - Rp^{n-1} - z}{p^{n+1} - 1}. \quad (24)$$

Consider a function of the form of (24), where the argument  $n$  varies continuously over a certain range

$$0 \leq n < N.$$

From Equation (24) we have:

$$\frac{dy_n}{dn} = \frac{(p-1)(pz-R)p^{n-1} \ln p}{(p^{n+1}-1)^2}. \quad (25)$$

$$\frac{d^2y_n}{dn^2} = \frac{-(p-1)(pz-R)p^{n-1}(p^{n+1}+1)\ln^2 p}{(p^{n+1}-1)^3}. \quad (26)$$

In the conditions under consideration  $p > 1$ ,  $R - pz < 0$ ,

we have from Equations (25), (26)

$$\frac{dy_n}{dn} > 0, \quad \frac{d^2y_n}{dn^2} < 0.$$

$y_n$  increases monotonically, and the graph of  $y_n$  (24) is convex. From (24):

$$\lim_{n \rightarrow +\infty} y_n = \frac{(z+R)p-R}{p^2} = y_0. \quad (27)$$

The graph of  $y_n$  (24) is plotted in Fig. 3.

The concentration in the last section of the extractor conforms to the inequality

$$y_n < \frac{(z+R)p-R}{p^2}. \quad (28)$$

There refers to the first assumption (12)

$$py_1 - R > 0,$$

a consequence of which is the consecutive increase of the acetic acid concentration from one section of the extractor to the next. It follows from Equations (6) that:  $y_1 < y_2 < y_3 \dots < y_n$ .

We now consider the other possible cases:

$$py_1 - R = 0, \quad (29)$$

$$py_1 - R < 0. \quad (30)$$

If Equation (29) holds,  $y_1$  is constant at constant  $\underline{k}$  and  $x_0$ . From Equations (5) we have

$$y_1 = \frac{x_0}{k}. \quad (31)$$

From Equation (16) and (17) when  $p > 1$

$$y_1 = y_2 = \dots = y_n = z = \frac{x_0}{k}. \quad (32)$$

Then in Equation (17)

$$R - pz = 0.$$

and

$$z = \frac{x_0}{k};$$

the last also follows from Equation (15).

Equation (32) has a perfectly definite meaning. It follows from this equation that the ratio  $\frac{x_0}{k}$  increases at constant  $x_0$  with decrease of the distribution coefficient of acetic acid between the nonaqueous and aqueous phases, and therefore the acetic acid content of the aqueous phase leaving the extractor increases. With prolonged use of the solvent, even if its acidity is constant, as  $\underline{k}$  decreases an instant may be reached when the ratio  $\frac{x_0}{k}$  is equal to  $z$ , the acetic acid concentration of the liquid feed. An increase of  $\frac{x_0}{k}$  is also possible with constant  $\underline{k}$ , as the result of an increase in the content, in the solvent of complex compounds of acetic acid with various impurities in the solvent. In either case a point is reached beyond which the solvent ceases to extract acetic acid from one phase into the other, and the acid concentration becomes the same in all the sections in the aqueous phase. In practical conditions (with correct control of extractor operation) such a situation is impossible in the course of normal extraction. In accordance with the direction in which acetic acid passes from one phase into the other, one or the other of the following inequalities must always hold:

$$y_1 > \frac{x_0}{k} \quad \text{or} \quad y_1 < \frac{x_0}{k}. \quad (33)$$

The inequality

$$y_1 < \frac{x_0}{k} \quad (34)$$

holds in the above-mentioned case (30):

$$py_1 - R < 0.$$

Inequality (34)

$$y_1 < \frac{x_0}{k}$$

holds when the extractor operation is reversed, and the solute is extracted from the nonaqueous phase by the aqueous phase.

Investigation of the case (30)

$$py_1 - R < 0,$$

when

$$y_1 > y_2 > \dots > y_n$$

is quite analogous to (12), considered earlier

$$py_1 - R > 0;$$

and is therefore not considered here. The corresponding graphs are given (Figs. 4, 5).

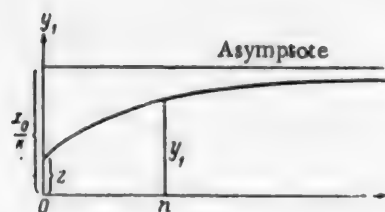


Fig. 4. Variation of the acetic acid concentration in the aqueous phase in the first section of the extractor when  $p > 1$  and  $y_1 < \frac{x_0}{k}$ .

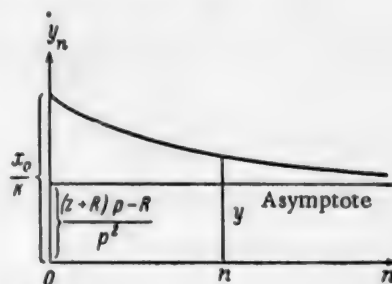


Fig. 5. Variation of the acetic acid concentration in the aqueous phase in the last section of the extractor when  $p > 1$  and  $y_1 < \frac{x_0}{k}$ .

#### SUMMARY

1. It is shown that the acetic acid concentration in the first section of the extractor, when  $x_0 \neq 0$ , conforms to the conditions:  $y_1 > \frac{x_0}{k}$  when acetic acid is extracted from the aqueous by the nonaqueous phase;  $y_1 < \frac{x_0}{k}$  for extraction from the nonaqueous by the aqueous phase; when no extraction occurs,  $y_1 = \frac{x_0}{k}$ .

2. It is shown that the acetic acid concentration in the aqueous phase in the last (top) section conforms to the inequalities:

$$\begin{aligned} \text{when } y_1 > \frac{x_0}{k}, \quad y_n &< \frac{(z+R)p-R}{p^2} \\ \text{when } y_1 < \frac{x_0}{k}, \quad y_n &> \frac{(z+R)p-R}{p^2} \end{aligned}$$

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## STUDY OF THE EXCHANGE-ADSORPTION PROPERTIES OF MONOCARBOXYCELLULOSE

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Studies of wood-cellulose preparations showed that it is impossible in practice to separate cellulose from its accompanying polysaccharides. For example, it is impossible to obtain cellulose preparations free from residual pentoses and uronic acids [1]. It follows that cellulose, and especially wood cellulose, preparations always contain some carboxyl groups. The presence of carboxyl groups in cellulose should have a definite influence on a number of its surface properties, including exchange adsorption of metal cations.

Our earlier papers [2] dealt with the exchange adsorption of cations on different types (sulfite and sulfate) of domestic wood cellulose and on cotton cellulose.

The purpose of the present investigation was to determine the influence of carboxyl group content on the exchange-adsorption properties of cellulose. Various samples of monocarboxycellulose [3] were used for the study. The samples were prepared by the selective oxidation, by means of gaseous nitrogen oxide, of the primary hydroxyl groups at the 6th carbon atom in the glucose residues of the cellulose macromolecules. The chemical properties of oxycelluloses (monocarboxycellulose) prepared by this method were studied by Rogovin [4], Sharkov [5], Kaverzneva [6], and their associates.

Decalcified bleached sulfite cellulose was used for the oxidation. The oxidation was performed by the static method [4] in a vacuum desiccator, with a weighing bottle containing liquid nitrogen tetroxide standing on its floor; the tetroxide rapidly evaporated at room temperature, and equilibrium became established in the desiccator between nitrogen dioxide and tetroxide. The degree of oxidation of cellulose, i.e., the number of carboxyl group at the 6th carbon atom in the glucose residue of the cellulose macromolecule, depends on the oxidation time, amount of nitrogen dioxide, and the temperature. After the oxidation, the unreacted nitrogen oxides were evacuated from the desiccator, and the monocarboxycellulose was thoroughly washed with distilled water until no longer acid to methyl orange. The preparations were then dried in the air at room temperature. This method was used to prepare four samples of monocarboxycellulose with different carboxyl group contents.

When cellulose is oxidized by nitrogen dioxide, mainly the primary groups at the 6th carbon atom are oxidized to carboxyl groups. At the same time, secondary alcohol groups evidently can also be oxidized to carboxyl groups to some extent. The strength of the carboxyl groups in oxycellulose may vary somewhat. The carboxyl groups at the 6th carbon atom, which are of the uronic acid type, are stronger than the carboxyl groups at the 2nd and 3rd carbon atoms [7].

Carboxyl groups are often determined quantitatively by decarboxylation under the action of heat and 12% hydrochloric acid [8]. However, this method only gives the content of the carboxyl groups at the 6th carbon atom; the carboxyl groups at the 2nd and 3rd carbon atoms are not decarboxylated under these conditions.

Methods for the determination of carboxyl groups, based on exchange adsorption, have recently come into use; in particular, the so-called "acetate method" is widely used. This method is based on a process of exchange adsorption involving hydrogen ions in the electrical double layer on the cellulose surface [9] and calcium ions in calcium acetate solution. Our earlier investigations showed [2] that the quantity of metal ions adsorbed by cellulose by the exchange mechanism depends on the pH of the equilibrium solution. There-

fore, the quantity of hydrogen ions displaced from the electrical double layer on the cellulose surface, which serves as a measure of the carboxyl group content of the given cellulose sample, also depends on the pH of the equilibrium solution.

When monocarboxycellulose comes in contact with calcium acetate solution, the equilibrium solution becomes acidified and the pH of the equilibrium solution is lower than the pH of the original solution. It must be emphasized that this pH decrease differs for different samples, and therefore replacement of hydrogen ions by calcium ions occurs at different pH values of the equilibrium solution. Data are presented below on the variations of the pH of acetate solution in contact with different samples of monocarboxycellulose with increasing carboxyl group contents.

It follows from Table 1 that the pH of the equilibrium solutions is lower than the pH of the original solutions in all cases, and the difference increases with increasing oxidation of the cellulose (the percentage of carboxyl groups). Since the magnitude of exchange adsorption greatly depends on the pH of the equilibrium solution, lower results are obtained for more highly oxidized than for less highly oxidized cellulose samples. For comparable results, the equilibrium solution pH must be the same for all the cellulose samples. This requirement is satisfied by our modification of the potentiometric method of carboxyl group determination described by Meesook and Purves [10]. The modified form of this method is as follows. Two potentiometric titration curves are obtained, one for the original 0.5 N calcium acetate solution, and the other for the same amount of the solution in presence of a weighed sample of oxycellulose. Curves for the amount of 0.1 N  $\text{Ca}(\text{OH})_2$  against pH are used to find the amount of calcium hydroxide required for the neutralization of the

TABLE 1

Variations of pH of the Acetate Solution in Contact with Monocarboxycellulose Samples

	Sample No.			
	1	2	3	4
pH of original 0.5 N calcium acetate solution	6.20	6.20	6.20	6.20
pH of equilibrium calcium acetate solution in contact with monocarboxycellulose	6.06	5.92	5.81	5.65

hydrogen ions displaced by calcium ions from the cellulose into solution at the required pH of the equilibrium solution. From this, the percentage content of carboxyl groups in the cellulose sample is calculated. A glass electrode was used for the potentiometric titration. In the titration in presence of cellulose, after the addition of each successive portion of calcium hydroxide the solution was shaken on the mechanical shaker until equilibrium was fully established (constant pH).

It is reported in the literature that determination of carboxyl groups in technical celluloses is difficult [11]. Therefore our results, which were obtained for a strictly definite pH value of the equilibrium solution (pH 7), may be regarded as the most reliable. Table 2 contains data on the carboxyl group contents of oxidized wood-cellulose samples, determined by decarboxylation with 12% HCl, by the usual acetate method, and by the potentiometric method at equilibrium pH = 7. The aldehyde group contents, determined from the iodine numbers at pH 9.2 in 0.05 M borax solution, are also given.

The fact that lower values are obtained for the carboxyl group content by the usual acetate method, with titration in presence of phenolphthalein, than by the potentiometric method is explained by the lower pH of the equilibrium solutions in the first method (see Table 1).

The discrepancy between the results obtained by the decarboxylation and the potentiometric methods probably indicates that when gaseous nitrogen dioxide acts on cellulose, not only the primary hydroxyl groups

TABLE 2

Carboxyl and Aldehyde Group Contents of Cellulose Oxidized by Nitrogen Dioxide

Method of determination	% contents of functional groups in monocarboxycellulose samples			
	1	2	3	4
Carboxyl groups, by decarboxylation with 12% HCl	2.98	5.05	6.78	18.62
Carboxyl groups, by acetate method (titration with phenolphthalein)	2.73	5.82	8.88	16.00
Carboxyl groups, potentiometrically at equilibrium pH 7	2.82	6.26	9.26	17.42
Aldehyde group, by iodine number	0.2	0.4	0.2	0.7

at the 6th carbon atom are oxidized, but the hydroxyls at the 2nd and 3rd carbon atoms are also affected to some extent. The amount of carboxyl groups at the 2nd and 3rd carbon atoms increases with the intensity of oxidation.

The adsorptive capacity of monocarboxycellulose was studied by the displacement method [2] in relation to divalent ions, and by the potentiometric method [12] in relation to monovalent ions. All the determinations were performed in duplicate. The differences generally did not exceed 1-2%, which is quite satisfactory for such a complex technical material as wood sulfite cellulose.

TABLE 3

Adsorption of Cupric, Calcium, and Barium Ions from 0.1 N solutions by Monocarboxycellulose Containing 2.8% Carboxyl Groups

Cu <sup>++</sup> ions		Ca <sup>++</sup> ions		Ba <sup>++</sup> ions	
pH	adsorption (in meq per 100 g of bone-dry cellulose)	pH	adsorption (in meq per 100 g of bone-dry cellulose)	pH	adsorption (in meq per 100 g of bone-dry cellulose)
1.12	8.8	1.22	4.0	2.03	11.8
1.62	8.1	2.16	12.4	2.77	24.2
2.00	14.1	2.84	22.2	3.47	37.1
2.32	20.5	3.56	39.8	4.14	47.1
2.62	27.3	3.88	46.8	4.72	50.0
3.22	41.2	4.49	50.5	5.93	52.8
3.72	48.8	5.18	52.4		
4.04	54.0	6.06	55.3		
4.52	60.6				
4.90	63.6				

TABLE 4

Adsorption of Cupric and Calcium Ions from 0.1 N Solutions by Monocarboxycellulose Containing 6.26% Carboxyl Groups

Cu <sup>++</sup> ions		Ca <sup>++</sup> ions	
pH	adsorption (in meq per 100 g of bone-dry cellulose)	pH	adsorption (in meq per 100 g of bone-dry cellulose)
1.08	7.9	1.99	23.9
1.60	18.7	2.85	50.6
2.05	38.3	3.46	81.6
3.22	110.9	4.54	106.1
3.99	148.9	5.99	112.4
4.22	153.9		
4.73	163.4		

Tables 3-7 contain data on the adsorption of various cations by monocarboxycelluloses with different carboxyl group contents, in relation to the pH of the equilibrium solution. For comparison, Table 8 contains corresponding values for adsorption on the original bleached sulfite cellulose which had been oxidized to the

TABLE 5

Adsorption of Cupric and Calcium Ions from 0.1 N Solutions by Monocarboxycellulose Containing 9.26% Carboxyl Groups

Cu <sup>++</sup> ions		Ca <sup>++</sup> ions	
pH	adsorption (in meq per 100 g of bone-dry cellulose)	pH	adsorption (in meq per 100 g of bone-dry cellulose)
1.12	13.7	1.18	13.6
1.54	34.3	2.07	45.7
1.90	69.1	2.68	94.8
2.17	94.1	3.44	154.9
2.30	103.9	3.95	186.8
2.58	133.2	4.73	189.6
3.10	178.7	5.29	193.8
3.57	220.8	5.40	195.5
3.87	229.8		
4.65	259.8		

TABLE 6

Adsorption of Cupric Ions from 0.1 N Solution by Monocarboxycellulose Containing 17.42% carboxyl Groups

pH	Adsorption (in meq per 100 g of bone-dry cellulose)
1.22	16.4
1.65	50.2
2.00	114.1
2.17	151.1
2.50	203.6
3.00	275.5
3.61	320.4
3.90	345.3
4.47	363.1

above-mentioned samples of monocarboxycellulose. The original sulfite cellulose contained 0.3% carboxyl groups, which evidently were formed as the result of oxidation during the bleaching of the pulp in course of production, and also included the carboxyl groups present in the native cellulose.

These data show that the adsorption of all cations increases sharply with increasing carboxyl group content in the cellulose macromolecule.

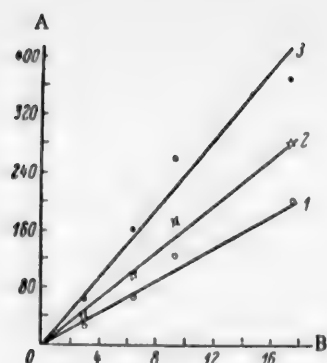
The graph shows the adsorption of cupric ions from 0.1 N solution by monocarboxycellulose, as a function of the carboxyl group content, for different pH values of the equilibrium solution (pH 2.5, 3.0, and 4.5).

TABLE 7

Adsorption of Lithium, Sodium, Potassium, and Ammonium Ions from 0.1 N Solutions by Monocarboxycellulose Containing 2.82% Carboxyl Groups

pH	Adsorption (in meq per 100 g of bone-dry cellulose)				pH	Adsorption (in meq per 100 g of bone-dry cellulose)			
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>		Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>
2.80	18.5	16.4	—	—	5.40	52.6	54.6	51.4	53.5
3.00	19.8	18.7	15.2	14.0	5.60	—	55.8	52.1	55.1
3.20	21.3	22.2	18.0	17.0	5.80	54.6	56.8	53.3	56.5
3.40	24.4	25.3	20.7	21.1	6.00	57.0	57.7	54.5	58.2
3.60	28.6	30.3	22.9	24.6	6.20	—	58.9	55.8	59.3
3.80	33.3	33.9	26.9	27.7	6.40	57.1	59.6	56.8	61.4
4.00	39.8	38.0	31.0	33.0	6.60	—	60.6	58.0	63.0
4.20	41.2	41.3	35.4	37.7	6.80	60.8	61.5	59.5	64.4
4.40	43.7	44.8	38.7	42.1	7.00	64.2	63.4	60.8	67.5
4.60	—	47.7	42.1	44.4	7.20	68.6	66.2	64.0	70.5
4.80	47.7	50.0	45.8	47.7	7.40	74.0	70.0	68.3	71.8
5.00	51.3	51.8	48.0	50.5	7.50	—	73.5	70.6	73.7
5.20	51.6	53.1	50.0	52.1					

It follows from the diagram that the adsorptive capacity of monocarboxycellulose is approximately proportional to its carboxyl group content. This confirms that the exchange-adsorption properties of cellulose samples are largely due to the presence of carboxyl groups. It must be pointed out, however, that the exchange-



Absorption of cupric ions on monocarboxycellulose samples with different carboxyl group contents, at various pH values. A) Adsorption (meq/100 g), B) carboxyl group content (%). pH: 1) 2.5, 2) 3.0, 3) 4.5.

ammonium ion is intermediate between the potassium and sodium ions, while at pH 6 and over it is ahead of lithium. Thus, the adsorption of the ammonium ion has certain specific characteristics.

TABLE 8

Absorption of Cupric Ions from 0.1 N Solution by Bleached, Decalcified Sulfite Cellulose

pH	Absorption of $\text{Cu}^{++}$ (in meq per 100 g bone-dry cellulose)
1.16	0.8
2.14	1.8
3.22	2.8
4.02	44.2
4.75	5.6

TABLE 9

Absorption of Cupric Ions by Monocarboxycellulose Containing 17.42% Carboxyl Groups, as a Function of the Cupric Ion Concentration in Equilibrium Solution, at Constant pH 2.7

Normality of equilibrium solution	Adsorption (in meq/100 g of bone-dry cellulose)		Deviation (%) $\frac{\Gamma_{\text{exp}} - \Gamma_{\text{calc}}}{\Gamma_{\text{exp}}} \cdot 100$
	found experimentally $\Gamma_{\text{exp}}$	calculated from the Langmuir eq. $\Gamma_{\text{calc}}$	
0.008	118.5	119.2	-0.6
0.100	234.4	242.8	-3.6
0.154	249.4	250.7	-0.5
0.255	258.6	256.8	+0.7
0.408	257.0	260.4	-1.3

Table 9 contains data on the adsorption of cupric ions by monocarboxycellulose containing 17.42% carboxyl groups (sample 4), in relation to the cupric ion concentration, at constant pH = 2.7. The adsorption at the same concentrations was calculated from the Langmuir equation. Table 9 shows that the Langmuir equation corresponds fairly satisfactorily to the isotherm for adsorption of cupric ions on monocarboxycellulose. The discrepancies between the experimental and calculated values in most cases do not exceed  $\pm 1\%$ , and only in one case, with 0.1 N solution, there is a deviation of -3.6%.

## SUMMARY

1. It is shown that in determinations of carboxyl groups in oxycelluloses, based on exchange adsorption, the pH of the equilibrium solution decreases and low values are therefore obtained for the carboxyl group contents. This error increases with increasing carboxyl group content in the cellulose. A potentiometric method is described for the determination of carboxyl groups in strongly oxidized celluloses, at strictly constant pH of the equilibrium solution.

2. The exchange-adsorption capacity of monocarboxy-celluloses, with different carboxyl group contents was studied in relation to univalent and bivalent ions in 0.1 N solutions at different pH values, and it was shown that the exchange-adsorption capacity of monocarboxy-cellulose is approximately proportional to the carboxyl group content. This indicates that the carboxyl group content of celluloses is one of the principal causes of their exchange-adsorption activity.

3. The Langmuir equation is shown to be applicable to the adsorption of cupric ions on monocarboxy-cellulose at constant pH of the equilibrium solution

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## BRIEF COMMUNICATIONS

### THE PREPARATION OF PHOSPHORUS THIOTRICHLORIDE

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Among the chemicals used for plant protection, an important place has been occupied in recent years by various esters of thiophosphoric acid; the main intermediate for the production of the latter is phosphorus thiotrichloride [1, 2]. Selection of a method for the production of phosphorus thiotrichloride is therefore of considerable importance. Several methods for the production of phosphorus thiotrichloride have been described in the literature; of these, the greatest practical interest attaches to methods based on the reaction of phosphorus trichloride with sulfur. As is known, the reaction between phosphorus trichloride and sulfur proceeds at elevated temperatures and under pressure, although it has been reported that it may take place in an open tube without the use of excess pressure [3]. The temperature of the reaction between sulfur and phosphorus trichloride can be lowered, and the process greatly accelerated, by the use of catalysts [4, 5]. Among the most noteworthy catalysts for this reaction are anhydrous aluminum chloride, ferric chloride, metal polysulfides, halogens, etc. [4-6]. In order to select a rational process for the production of phosphorus thiotrichloride, we studied the reaction of phosphorus trichloride with sulfur both in absence of catalysts, and in presence of various substances.

The reaction between phosphorus trichloride and sulfur in presence of anhydrous aluminum chloride and similar catalysts proceeds readily at the boiling point of phosphorus trichloride, and yields fairly pure phosphorus thiotrichloride. However, the yield of phosphorus thiotrichloride does not exceed 75-80%, and considerable amounts of double compounds of aluminum chloride with phosphorus trichloride and thiotrichloride, consisting of a thick mass difficult to remove from the reaction vessel, are formed as a by-product.

In our opinion, a more convenient method for the production of phosphorus thiotrichloride is by the reaction of sulfur with phosphorus trichloride in presence of metal polysulfides, although a higher temperature is needed for this reaction. We studied the kinetics of the reaction between sulfur and phosphorus trichloride at various temperature, in order to elucidate the reaction mechanism and to find the optimum process conditions.

TABLE 1

Reaction of  $\text{PCl}_3$  with Sulfur at  $160^\circ$

Time (min)	$n_D^{20}$	Amount of $\text{PSCl}_3$ form- ed (%)	$K_1 \cdot 10^4$
60	1.5433	53.5	3.2
120	1.5496	71.0	3.4
180	1.5512	76.5	3.1
240	1.5526	80.0	2.8

TABLE 2

Reaction of  $\text{PCl}_3$  with Sulfur at  $190^\circ$

Time (min)	$n_D^{20}$	Amount of $\text{PSCl}_3$ form- ed (%)	$K_1 \cdot 10^4$
15	1.5352	33.5	—
30	1.5468	63.0	9.6
60	1.5522	79.0	10.3
120	1.5536	86.5	8.7
240	1.5562	91.0	9.9

The experiments were performed in sealed molybdenum-glass tubes. An equimolecular mixture of phosphorus trichloride and sulfur was put into the tubes, which were heated in an air thermostat with temperature fluctuations of  $\pm 0.5^\circ$ . The contents of the tubes were agitated during the whole time of heating in the thermostat. At the end of a definite time the tubes were taken out of the thermostat, cooled for 15 minutes, opened, and

their contents analyzed. The phosphorus thiotrichloride content was determined from the refractive index; the refractive indices of mixtures of phosphorus thiotrichloride with phosphorus trichloride, and saturated solutions of sulfur in these mixtures, were first determined for this purpose. Variations of the refractive index with the composition of the mixtures are plotted in Fig. 1.

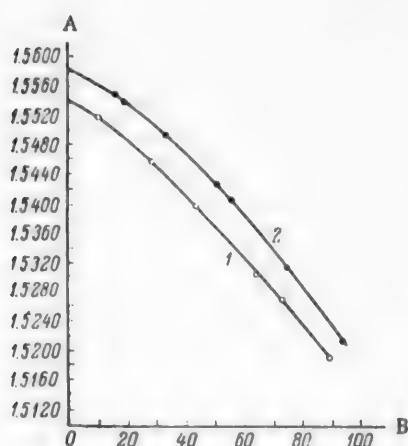
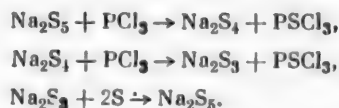


Fig. 1. Variation of the refractive index of mixtures with the composition. A) Refractive index at 20°, B) PCl<sub>3</sub> content in mixture with PSCl<sub>3</sub> (%). Curves: 1) mixture of PCl<sub>3</sub> with PSCl<sub>3</sub>; 2) saturated solution of sulfur in a mixture of PCl<sub>3</sub> and PSCl<sub>3</sub>.

at 160 and 190° is fairly considerable; the reaction is of the second order. However, it is difficult to carry out a continuous process at this reaction rate, as the volume of the reaction equipment must be rather large. It should be noted that the error in the individual experiments may be fairly considerable (5-7%). This is because sealed tubes and increased pressures and temperatures have to be used. The errors are caused mainly by differences in the temperature conditions at the initial and final stages of the process. Errors of this type are probably unavoidable in experiments with corrosive volatile substances at elevated temperatures and pressures.

Special experiments showed that the rate of reaction between phosphorus trichloride and sulfur is nearly trebled in presence of sodium or potassium polysulfide. The alkali-metal polysulfide apparently acts as a sulfur carrier, as shown below:



To test this hypothesis, experiments were performed on the reaction of sodium penta- and tetrasulfide with phosphorus trichloride. These experiments showed that the reaction between sodium polysulfides and phosphorus trichloride proceeds even at 100° and is almost complete in 1 hour. These results fully confirm the reaction mechanism postulated above.

The following technological process is recommended, on the basis of these results, for the production of phosphorus thiotrichloride from sulfur and phosphorus trichloride (Fig. 3). The steel reaction towers 1, fitted with bubbling devices, are charged with 0.5-3.5% solution of anhydrous sodium sulfide in sulfur, and phosphorus trichloride vapor is bubbled through the melted mass at 160-180°. Phosphorus trichloride is forced by nitrogen pressure from the vessel 2 into the measuring tank 3, and then into the evaporator 4, heated by flue gas. From the evaporator 4 the phosphorus trichloride vapor enters the towers 1 and passes through the melted layer of sulfur; the phosphorus thiotrichloride formed is condensed in the steel air condensers 5. The condensate then

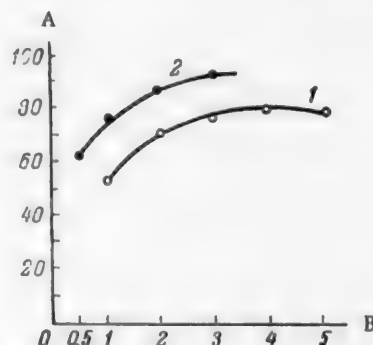


Fig. 2. Kinetics of the PCl<sub>3</sub> - sulfur reaction. A) Amount of PSCl<sub>3</sub> (%), B) time (hours). Temperature (in °C): 1) 160, 2) 180.

The rate of the sulfur-phosphorus trichloride reaction is low at 100°, as only about 4% of the sulfur reacts in 5 hours. Kinetic data for the sulfur-phosphorus trichloride reaction at 160° are given in Table 1, and at 190°, in Table 2. It is seen that the rate of the sulfur-phosphorus trichloride reaction

passes to the receivers 6 and the still 7. Part of the distilled unreacted phosphorus trichloride is recycled. The sulfur in the towers is replaced as consumed, by the addition of a sulfur solution in a mixture of phosphorus thio-trichloride and phosphorus trichloride (40%: 60%), at an elevated temperature and under some excess pressure, from the measuring vessel 8.

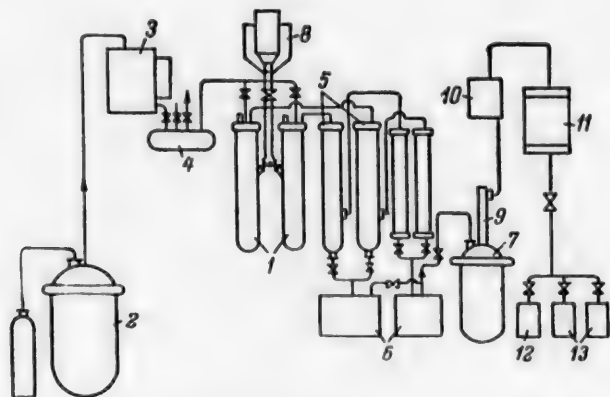


Fig. 3. Technological process for the production of phosphorus thiotrichloride. 1) Reaction towers, 2)  $\text{PCl}_3$  receiver, 3) measuring tank for  $\text{PCl}_3$ , 4)  $\text{PCl}_3$  evaporator, 5) air condenser, 6) condensate receivers, 7) still, 8) measuring vessel for sulfur solution, 9) rectification column, 10) dephlegmator, 11) condensers, 12) receiver for 1st fraction, 13) receiver for  $\text{PSCl}_2$ .

This process has been in use since 1950 for the production of phosphorus thiotrichloride in one of the chemical works.

The yield of phosphorus thiotrichloride is 95-96%, and the conversion of  $\text{PCl}_3$  to  $\text{PSCl}_2$  is from 80 to 97% (according to the output rate required).

#### SUMMARY

1. The kinetics of the sulfur-phosphorus trichloride reaction at 160 and 190° was studied, and it was shown that alkali-metal polysulfides catalyze the reaction. The mechanism of the catalytic action of the polysulfides was studied.

2. A continuous process for the production of phosphorus thiotrichloride is proposed.

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\*In Russian.

# EFFECT OF THE VELOCITY GRADIENT ALONG THE AUTOCLAVE RADIUS IN LAMINAR FLOW OF THE PULP ON THE YIELD OF ALUMINA IN ALKALINE LEACHING OF BAUXITE

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In alumina production, the wet grinding of bauxite in ball mills with recycled alkali yields a pulp which is then heated to a high temperature and treated in autoclaves to dissolve the hydrated alumina diaspore or boehmite present in the ore. In relation to a continuous process of bauxite leaching, it was necessary to study the course of this process with laminar flow of the pulp through continuous-action autoclaves. One possible form of the continuous autoclave can be considered as a wide pipe through which bauxite pulp flows in a laminar stream. We were unable to find in the literature a method for determination of the extent of reaction in laminar flow.

The calculations were performed for ideal conditions, in which the dissolution kinetics of  $Al_2O_3$  present in the bauxite grains is the same in the continuous and in the batch process, although the latter is carried out in an autoclave with forced agitation of the pulp. This assumption is justified to some extent, as the displacement of the liquid medium, caused by turbulent pulsations, relative to the fine bauxite particles suspended in the viscous alkaline solution may be ignored, and it may be assumed that the particles are extracted in a medium which may be considered stationary [1, 2].

The following notation is used:  $H$  is the autoclave height (dm),  $R$  is the autoclave radius (dm),  $r$  is the radius of an elementary annular layer (dm),  $w$  is the linear velocity of the pulp in the elementary layer (dm/hour),  $w_0$  is the average velocity of the pulp (dm/hour),  $\tau$  is the time during which the elementary volume of the pulp remains in the autoclave (hours),  $Q$  is the pulp flow rate (liters/hour),  $M$  is the amount of alumina extracted from the bauxite (kg/hour),  $A$  is the  $Al_2O_3$  content of the bauxite (in fractions of unity), and  $C$  is the bauxite content of the pulp (kg/liter).

The kinetics of batch leaching of bauxite without addition of lime\* is represented by the equation

$$q = \frac{b}{k} \left( 1 - 10^{-\frac{kt}{2.3}} \right), \quad (1)$$

where  $t$  is the leaching time, and  $b$  and  $k$  are constants which depend on the nature of the bauxite, its degree of subdivision, and the undersaturation of the original recycled alkali with respect to  $Al_2O_3$ .

$$\frac{b}{k} = \frac{Al_2O_{3sat} - a}{m},$$

where  $Al_2O_{3sat}$  is the  $Al_2O_3$  concentration of the saturated equilibrium solution (g/liter),  $a$  is the  $Al_2O_3$  concentration of the recycled alkali used for the bauxite leaching (g/liter),  $m$  is the bauxite  $Al_2O_3$  content of the pulp (g/liter).

\*Lime accelerates the leaching of diaspore bauxites.

Therefore  $b/k$  is the ratio of the maximum amount of  $Al_2O_3$  which can be dissolved in 1 liter of the solution, to the amount of bauxite  $Al_2O_3$  per liter of solution in the pulp.

If the leaching is performed in an "ideal displacement" apparatus (Fig. 1), the amount of  $Al_2O_3$  entering the solution depends on the time:  $\tau_0 = \frac{H}{w_0}$ . In laminar flow, illustrated in the same diagram, the velocity of different layers of the pulp is a function of  $r$ .

$$w = 2w_0 \left(1 - \frac{r^2}{R^2}\right) = \frac{2H}{\tau_0} \left(1 - \frac{r^2}{R^2}\right). \quad (2)$$

The amount of pulp flowing through an elementary annular layer of cross section  $2\pi r dr$  is  $dQ = 2\pi w r dr$ ; the amount of alumina extracted from it is

$$dM = 2\pi C A w q r dr.$$

Substitution of the values of  $q$  and  $w$  from Equations (1) and (2) into this last expression gives:

$$dM = 2\pi C A \frac{2H}{\tau_0} \left(1 - \frac{r^2}{R^2}\right) \cdot \frac{b}{k} \left(1 - 10^{-\frac{kt}{4.6}}\right) r dr. \quad (3)$$

In Equation (3)  $t = \frac{H}{w}$ , and in view of Equation (2)

$$t = \frac{H}{w} = \frac{\tau_0}{\left(1 - \frac{r^2}{R^2}\right)}. \quad (4)$$

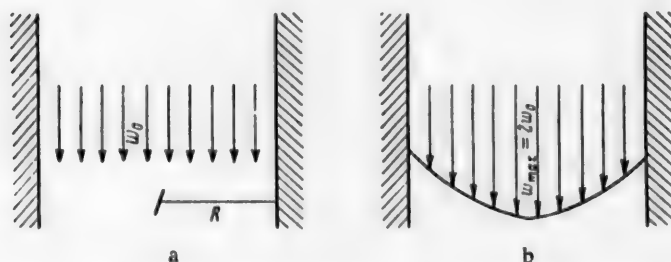


Fig. 1. Flow in an "ideal displacement" apparatus a, laminar flow in the apparatus b.

The total extraction of bauxite in an autoclave with laminar pulp flow is

$$x = \frac{\int_0^R dM}{QCA}, \quad (5)$$

where  $Q = \frac{\pi R^2 H}{\tau_0}$ .

Substituting into Equation (5) the value of  $dM$  from Equation (3), where  $t$  is taken from Equation (4), we have

$$x = \frac{4b}{R^4 k} \left[ \frac{R^4}{4} + \int_0^R r^3 \cdot 10^{-\frac{k\tau_0}{4.6 \left(1 - \frac{r^2}{R^2}\right)}} dr - R^2 \int_0^R r \cdot 10^{-\frac{k\tau_0}{4.6 \left(1 - \frac{r^2}{R^2}\right)}} dr \right]. \quad (6)$$

From Equation (6), when  $t_0 \rightarrow \infty$ ,  $q = \frac{b}{k}$ . Therefore, if the autoclave is very long, the yield in laminar flow becomes equal to the yield in a batch autoclave with infinite leaching time.

The numerical values of the functions

$$f(r) = r^3 \cdot 10^{-\frac{k\tau_0}{4.6\left(1-\frac{r^4}{k^2}\right)}},$$

$$F(r) = r \cdot 10^{-\frac{k\tau_0}{4.6\left(1-\frac{r^4}{k^2}\right)}},$$

are plotted against various values of  $r$ . The areas under these curves give the integrals in Equation (6).

These values are:

	1 hours	2 hours	3 hours
$\int_0^R f(r) dr$	$0.0915 R^4$	$0.05 R^4$	$0.028 R^4$
$R^3 \int_0^R F(r) dr$	$0.0252 R^4$	$0.152 R^4$	$0.09 R^4$

These values of the integrals were used to calculate the amount of  $Al_2O_3$  passing from the bauxite into solution.

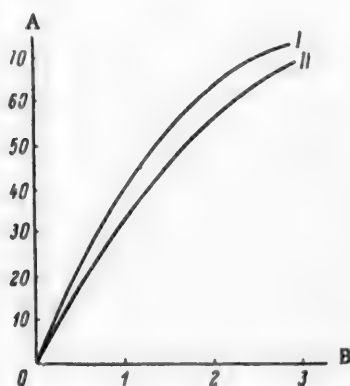


Fig. 2. Kinetics of bauxite leaching. A) Yield of  $Al_2O_3$  (%), B) time (hours). I) Batch process, II) continuous process in laminar flow.

The kinetics of bauxite leaching in laminar flow of the pulp through the autoclave can be represented by Curve I in Fig. 2. The curve for the kinetics of bauxite leaching in a batch autoclave is shown in the same diagram. It is seen that the kinetics of bauxite leaching without addition of lime, with laminar flow of the pulp through the autoclave, differs appreciably from the kinetics of the batch process. If several autoclaves are used, they must be connected by pipes in which the different layers become mixed; moreover, laminar flow is not established immediately the pulp enters the autoclave, and for some time the velocity of the pulp is the same across the autoclave. These factors should increase the extraction of  $Al_2O_3$  into solution during leaching of bauxite in laminar flow. Diffusional displacement of the dissolved  $Al_2O_3$  across the autoclave is also ignored in the calculation.

This correction is very small, because the flow rate is immeasurably greater than the diffusion rate. The relative displacement of the solid particles in the pulp is also disregarded; the resultant error is not large if the bauxite does not contain large particles ( $+100 \mu$ ). The actual difference between the alumina extraction in batch leaching of bauxite, and in continuous leaching with laminar flow of the pulp, found to be 3-4%, is close to the calculated value.

#### SUMMARY

A method for calculation of yields in laminar flow of liquids through reactors is demonstrated by the example of bauxite leaching in an autoclave with laminar flow of the pulp.

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\*In Russian.

## EFFECT OF HYDROGEN-ION CONCENTRATION ON THE EXTRACTION OF COLLOIDS FROM SOLUTIONS WITH THE AID OF FOAM

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The extraction of substances from solution with the aid of foam depends on a number of factors.

Mokrushin and Potaskuev [1] showed that the degree of extraction varies with the amount of foam former (gelatin). There is an optimum gelatin concentration at which the maximum extraction is obtained.

One important factor determining the foaming power of gelatin is the hydrogen-ion concentration. It follows that this factor should be expected to influence the extraction process. Schutz [2] studied the effect of hydrogen-ion concentration on the hardness of films in protein foams, and found that the most favorable conditions for protein fractionation correspond to the isoelectric point.

The state of gelatin greatly depends on the hydrogen-ion concentration [3]. At  $\text{pH} < 4.7$  gelatin is positively charged, whereas at  $\text{pH} > 4.7$  it is negatively charged. Moreover, the pH influences the surface activity of gelatin. Its surface activity is greatest at the isoelectric point ( $\text{pH} = 4.7-4.8$ ).

The present paper deals with a study of the effect of hydrogen-ion concentration on the extraction of the disperse phase from a number of hydrosols by means of gelatin foam.

The following sols were used in the investigation: antimony sulfide, gold, ferric hydroxide, and titanium hydroxide.

The hydrogen-ion concentration was varied by additions of nitric acid or caustic soda. The pH was determined by means of an electronic pH meter of the LLPU-1 type, with a glass electrode.

The experimental procedure was as follows. 100 ml of the sol with appropriate addition of acid or alkali and 1% gelatin solution was put into a vertical tube with a porous bottom. When dispersed air was blown through the solution, foam was formed which entrained the colloidal particles. Samples were taken, at equal time intervals, for determination of the degree of extraction by means of the photoelectric colorimeter.

Let us consider the experiments with colloidal antimony sulfide solution. The pH of the original solution was 4.4. The hydrogen-ion concentration was varied in the direction of increasing acidity.

The results of the experiments are given in Fig. 1.

The degree of extraction of the colloid decreased as the solution pH was changed from 4.4 to 2.7. On further decrease of pH to 2.1, the extraction increased.

It should be noted that the nature of the foam also changed with increase of the hydrogen-ion concentration. The foam became more finely cellular and moist, and the height of the foam column increased.

Gold hydrosol was studied over a wider pH range.

Figure 2 shows that the degree of extraction decreases with increase of hydrogen-ion concentration to  $\text{pH} = 3.3$ , while on further increase of the hydrogen-ion concentration to  $\text{pH} = 2.8, 2.0, 1.5$  the extraction increases.

Changes of pH toward the alkaline, to 6.2 and 8.0 resulted in decreased extraction, but at pH = 10 the extraction of colloidal gold was somewhat increased again.

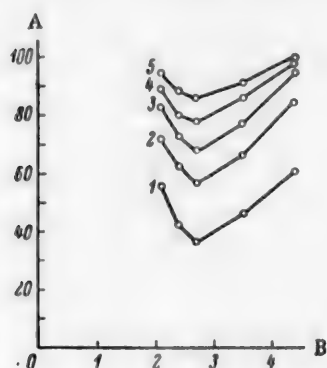


Fig. 1. Effect of hydrogen-ion concentration on the extraction of 0.005% colloidal  $\text{Sb}_2\text{S}_3$ . A) Amount of  $\text{Sb}_2\text{S}_3$  extracted (%), B) pH. Extraction time minutes: 1) 3, 2) 6, 3) 9, 4) 12, 5) 15.

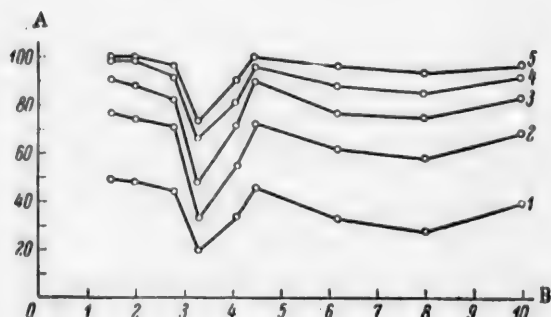


Fig. 2. Effect of hydrogen-ion concentration on the extraction of colloidal Au. A) Amount of Au extracted (%), B) pH. Extraction time (minutes): 1) 3, 2) 6, 3) 9, 4) 12, 5) 15.

The results of experiments with ferric hydroxide sol are given in Fig. 3.

It is seen that the curves for the extraction as a function of the hydrogen-ion concentration have maxima in the region pH = 5.0, and the extraction decreases gradually on further increase of pH.

Similar results were obtained in experiments with titanium hydroxide sol.

Figure 4 shows that the maximum extraction is obtained in the region of pH = 4.8. The degree of extraction decreases on further decrease of the hydrogen-ion concentration.

In analysis of the experimental results, it is necessary to consider the simultaneous influence of hydrogen ions on the foaming agent (gelatin) and on the sol.

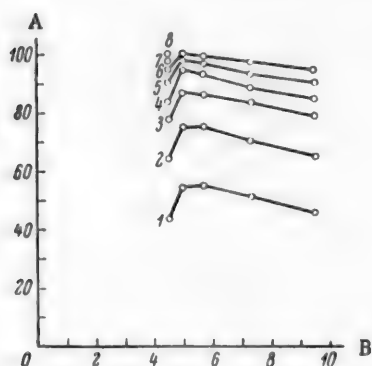


Fig. 3. Effect of hydrogen-ion concentration on the extraction of colloidal  $\text{Fe}(\text{OH})_3$ . A) Amount of  $\text{Fe}(\text{OH})_3$  extracted, B) pH. Extraction time minutes: 1) 3, 2) 6, 3) 9, 4) 12, 5) 15, 6) 18, 7) 21, 8) 24.

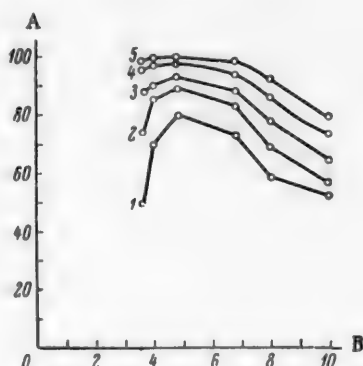


Fig. 4. Effect of hydrogen-ion concentration on the extraction of colloidal  $\text{Ti}(\text{OH})_4$ . A) Amount of  $\text{Ti}(\text{OH})_4$  extracted, B) pH. Extraction time minutes: 1) 3, 2) 6, 3) 9, 4) 12, 5) 15.

It is known that when the pH does not correspond to the isoelectric state of gelatin, the latter undergoes either acidic or basic dissociation. The ions formed are hydrated more strongly than undissociated gelatin molecules. This may account for the observed increased moisture content of the foam when the pH was changed in the acid or alkaline direction.

On the other hand, increased hydration of gelatin influences the degree of extraction of colloids by foam. Strong hydration makes ionized gelatin less accessible to colloidal particles, and hinders its passage to the liquid-gas interface. Conversely, at the isoelectric point ( $\text{pH} = 4.7-4.8$ ) the hydration of gelatin is least and its surface activity is highest; i.e., it passes readily to the interface.

This explains why near  $\text{pH} = 4.8$ , i.e., near the isoelectric point of gelatin, maximum extraction was obtained in these experiments. Under these conditions, gelatin, like other protein substances, forms the most stable films; this is noted by Cumper [4].

The degree of extraction is a direct function of film strength.

Moreover, the sensitizing role of gelatin should be noted. Since the amount of gelatin added is small, the colloidal particles group around its molecules, and not the other way about.

This aggregation of the colloidal particles tends to increase the degree of extraction.

In the low and high pH regions, as at the isoelectric point, film stability increases. Further, the influence of the sensitization factor increases under these conditions.

All this accounts for the observed increases in the extraction of colloidal antimony sulfide and gold at low and high pH values. It should be noted, however, that the extraction of colloidal particles of ferric and titanium hydroxides, which are somewhat hydrophilic, was less at high pH values, in contrast to the hydrophobic gold particles. Consequently, the hydrophily of the colloidal particles is also significant in these effects.

#### SUMMARY

1. The hydrogen-ion concentration has a considerable influence on the extraction of the disperse phase from hydrosols.
2. The maximum degree of extraction of colloids in foam occurs in the pH region corresponding to the isoelectric state of gelatin.
3. At low pH the degree of extraction of colloidal  $\text{Sb}_2\text{S}_3$  and Au increases. At high pH ( $\text{pH} 10$ ) an increase in the extraction was found only in the case of colloidal Au particles, whereas the extraction of  $\text{Fe}(\text{OH})_3$  and  $\text{Ti}(\text{OH})_4$  particles, which are somewhat hydrophilic, decreases at this pH.

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# CALCULATION OF ELECTROCHEMICAL PROTECTION WITH FIELD INTERACTION IN THE ELECTROLYTE TAKEN INTO ACCOUNT

V. V. Gerasimov

Electrochemical protection is coming into increased use in the national economy. However, there is as yet no rational calculation method for precise determination of the protecting electrode dimensions and their location for complete protection of metal constructions.

The distribution of potentials in the electrolyte and at the electrode surfaces can be found by solution of the Laplace equation for nonlinear boundary conditions. However, the solution of this problem involves very great difficulties, and can be completed only in rare instances [1-3].

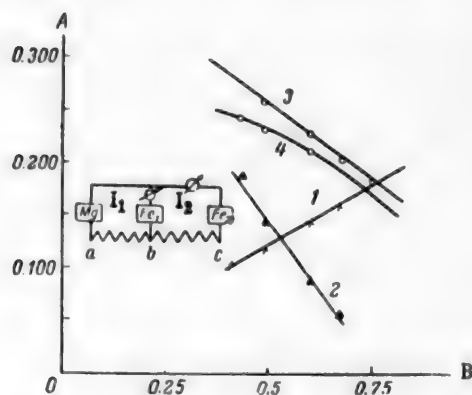


Fig. 1. Calculated and experimental values of the ohmic drop of potential between magnesium and iron electrodes ( $\text{Fe}_2$  in the diagram). A) Ohmic potential drop  $\Delta v_r$  (V), B) current strength  $I_2$  (ma). Curves: 1)  $\Delta v_r$  calculated for  $\text{Fe}_2$  with field interaction disregarded; 2)  $\Delta v_r$  calculated for  $\text{Fe}_1$  with field interaction disregarded; 3)  $\Delta v_r$  calculated for  $\text{Fe}_2$  with field interaction taken into account; 4)  $\Delta v_r$  for  $\text{Fe}_2$ , determined experimentally.

A system of a magnesium specimen and two iron specimens (circuit diagram in Fig. 1) was considered for quantitative evaluation of field interaction in the electrolyte, and calculation of the ohmic drop of potential in the electrolyte. The ohmic drop of potential between the magnesium and the iron specimen 2, i.e., the potential difference  $\Delta v_{rac}$  between the points a and c, is

$$\Delta v_{rac} = v_c - v_a = (v_c - v_b) - (v_b - v_a) = \Delta v_{rbc} + \Delta v_{rab}, \quad (1)$$

This paper constitutes an attempt to devise a simple approximate calculation method for electrochemical protection systems. The calculation is based on Akimov's theory of multielectrode systems [4].

Calculations relating to electrochemical protection systems regarded as multielectrode systems are difficult because in such a system some of the electrodes are polarized completely, some partially, and some are not polarized at all.

Cases of either completely polarized or completely unpolarized systems have been worked out in detail.

Akimov [4] demonstrated for binary models of corrosion cells that polarizational potential drop can be summated with ohmic potential drop ( $\Delta v_r$ ). If several galvanic cells are in operation, the electrical fields in the electrolyte are superposed, with corresponding changes in the current flowing in these cells; the current may be either mutually weakened, or intensified.

A system of a magnesium specimen and two iron specimens (circuit diagram in Fig. 1) was considered for quantitative evaluation of field interaction in the electrolyte, and calculation of the ohmic drop of potential in the electrolyte. The ohmic drop of potential between the magnesium and the iron specimen 2, i.e., the potential difference  $\Delta v_{rac}$  between the points a and c, is

$$\Delta v_{r_{be}} = r_{be} \cdot I_2, \quad (2)$$

$$\Delta v_{r_{ab}} = r_{ab} (I_1 + I_2) = r_{ab} \cdot I_2 + r_{ab} \cdot I_1, \quad (3)$$

$$\Delta v_{r_{ae}} = (r_{ab} + r_{be}) I_2 + r_{ab} I_1 = \Delta v_{r_2} + \Delta v_{r_1}. \quad (4)$$

The Lines 1 and 2 in Fig. 1 represent the variations of  $\Delta v_{r_2}$  and  $\Delta v_{r_1}$  with the current  $I_2$ . Line 3 is obtained by summation of Lines 1 and 2, and represents values of  $\Delta v_{r_{ab}}$  calculated from the values of the electrolyte resistance between the electrodes, and the current strengths. Curve 4 represents the corresponding experimental values. It is clear from Fig. 1 that the agreement between the experimental and calculated values is satisfactory.

Consider the calculation of an electrochemical protection scheme for a unidimensional case. The protected construction is divided into  $n$  equal regions. Let the distance between the centers of two adjacent regions be  $l_1$ . The distance between the protecting anode and the 1-th region is

$$l_i = l_1 \cdot i. \quad (5)$$

The circuit diagram for such a system is given in Fig. 2, where  $r_a$  is the polarization resistance of the magnesium, and  $r_c$  is the polarization resistance of a region of the protected construction. At the potentials

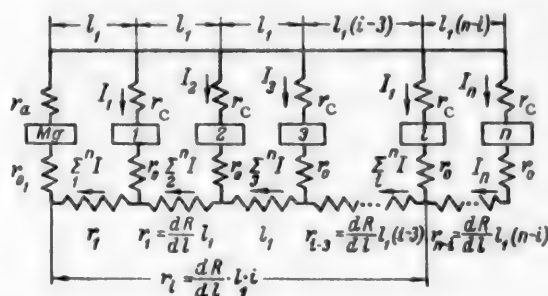


Fig. 2. Circuit diagram for calculation of an electrochemical protection system.

usual in electrochemical protection, both these values can be assumed, according to our data, to be independent of current density. As was shown earlier [5], the electrolyte resistance between two electrodes can be separated into two parts: one depends on the electrode areas  $r_0$  and  $r_{01}$ , and the other depends on the distance between the electrodes.

$$r_i = \frac{dR}{dl} \cdot l_i. \quad (6)$$

By Kirchhoff's second law, we have for the contour of the first region

$$E_{Fe}^0 - E_{Mg}^0 = E_1^0 = r_a \sum_1^n I_i + I_1 r_{c1} + I_1 r_0 + \frac{dR}{dl} l_i \sum_1^n I_i + r_{01} \sum_1^n I_i; \quad (7)$$

for the second

$$E_2^0 = r_a \sum_1^n I_i + I_2 r_c + r_0 I_2 + \frac{dR}{dl} 2l_i \sum_2^n I_i + \frac{dR}{dl} l_1 I_1 + r_{01} \sum_1^n I_i; \quad (8)$$

for the third

$$E_3^0 = r_a \sum_1^n I_i + I_3 r_c + r_0 I_3 + \frac{dR}{dl} 3l_i \sum_3^n I_i + \frac{dR}{dl} l_1 I_1 + \frac{dR}{dl} 2l_{01} \cdot I_2 + r_{01} \sum_1^n I_i; \quad (9)$$



and for the  $i$ -th region

$$E_i^0 = r_a \sum_1^n I_i + I_i r_c + I_i r_0 + \frac{dR}{dt} \cdot i \cdot l_1 \sum_1^n I_i + \sum_1^{i-1} \frac{dR}{dt} l_1 (i-1) I_i + r_0 \sum_1^n I_i. \quad (10)$$

We solve a system of  $n$  equations with  $n$  unknowns to find  $I_1, I_2, I_3, \dots, I_1 \dots I_n$ , and, from the known polarization resistances  $r_c$ , we also find the potentials at the different regions of the protected construction.

If the length of the construction is great,  $n$  is also great. Solution of a system of  $n$  equations with  $n$  unknowns is simpler than solution of the Laplace equation, but nevertheless it involves certain difficulties. The calculation may be simplified considerably without undue loss of accuracy. For this, the construction is first divided into 4 equal regions, and  $I_1, I_2, I_3$ , and  $I_4$  are found. The region nearest to the protector is then itself divided into four regions. The solution of four equations with four unknowns does not present any difficulties.

Because of the low polarizability of magnesium,  $r_a$  was assumed to be 0.

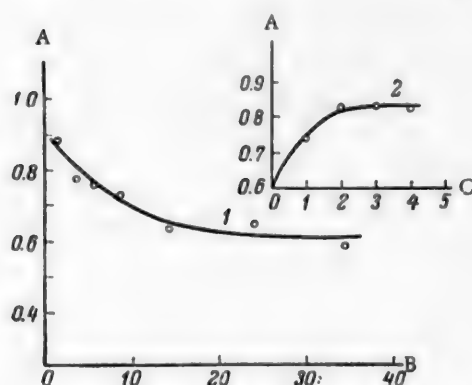


Fig. 3. Potential distribution along a protected block in 0.012% sodium chloride after 3 days of immersion. Area of the protected surface 96 cm<sup>2</sup>. Protecting anode area 8 cm<sup>2</sup>. A) Negative potential  $E$  (in v), B) length (cm), C) time (days). 1) Calculated values, 2) change of potential with time, at a distance of 5.85 cm from the protecting anode (determined by means of a saturated calomel electrode). Experimental results indicated by circles.

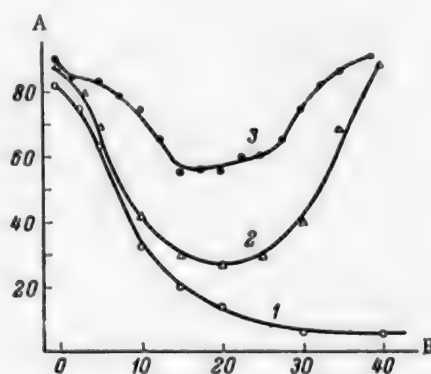


Fig. 4. Current-density distribution along a protected rod. A) Current density (ma/cm<sup>2</sup>), B) length (cm). Curves: 1) Experimental; one protecting anode at cathode end; 2) calculated on the basis of simple summation of the currents from two protecting anodes at the cathode ends, with field interaction in the electrolyte disregarded; 3) experimental; a protecting anode at each end of the cathode.

Figure 3 shows the calculated potential distribution over the surface of a protected steel block, and also several experimental values for the potentials along the block. It is seen from Fig. 3 that the agreement between the calculated and experimental data is good.

In conclusion, we consider one more aspect of field interaction in the electrolyte. If a protecting anode is connected to one end of a rod 40 cm long, the current-density distribution along it is represented by Curve 1 in Fig. 4.

Let a similar anode be connected to the other end of the rod. If we assume that the protective currents from the two protecting anodes are additive, the current-density distribution along the rod should be represented by Curve 2 in Fig. 4. The experimental values are represented by Curve 3.

Mutual intensification of protective currents under the influence of field interaction takes place in this case.

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# NATURE OF THE INFLUENCE OF THE pH OF THE MEDIUM ON THE CORROSION OF IRON IN PRESENCE OF INHIBITORS

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Iron dissolves in media of fairly high acidity mainly by hydrogen depolarization, without formation of insoluble compounds [1]. Under such conditions the role of pH in iron corrosion should be determined largely by its influence on hydrogen evolution.

This paper contains certain experimental data obtained in a study of the effect of pH of the medium on the corrosion rate of iron. Pure hydrochloric acid, and acid containing anthranilic acid and tetrabutylammonium sulfate, were used for the experiments. The corrosion rate was usually determined from the weight loss of the specimen, and was expressed in current-density units

(amp/cm<sup>2</sup>). Preliminary experiments showed that the results given by the gravimetric and volumetric methods diverge only for weakly acidic solutions (pH = 0.61 and 1.06) containing tetrabutylammonium sulfate, because of the increased role of oxygen depolarization. Therefore in this case the corrosion rate was calculated from the volume of hydrogen liberated. The solution pH was determined by means of a glass electrode with a tube amplifier type LU-2; the pH was also checked before and after the experiment. The experiments were performed in an air thermostat at 20 ± 0.5°. The duration of each experiment was 24 hours.

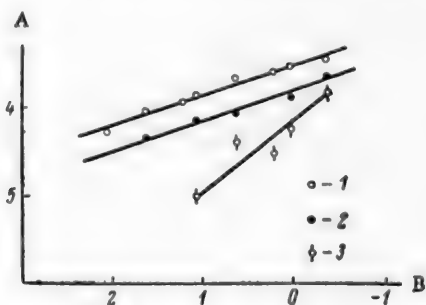


Fig. 1. Effect of hydrogen-ion concentration on the corrosion rate of iron in hydrochloric acid. A)  $\log i_{\text{corr}}$ , B)  $\log C_{\text{H}^+}$ . 1) Without additions; 2) with 0.1 g of anthranilic acid per liter, 3) with 1.0 g of tetrabutylammonium sulfate sulfate per liter.

The experimental results give satisfactory linear plots in  $\log i$ -pH coordinates (Fig. 1), and can be represented by Equation (1)

$$\log i = \log i_0 - \gamma \cdot \text{pH}, \quad (1)$$

where  $i$  and  $i_0$  are the corrosion rates at the given pH and pH = 0 respectively, and  $\gamma$  is the slope of the line relative to the pH axis.

For hydrochloric acid solutions,  $\gamma$  is 0.31, which is in good agreement with published data [2, 3]. The corrosion rate is decreased by addition of anthranilic acid; its inhibitory effect is almost independent of pH, and the slope of the  $\log i$ -pH plots remains the same as for hydrochloric acid solutions without additive. On the other hand, the action of tetrabutylammonium sulfate depends on the solution pH, and although the relationship between  $\log i$  and pH remains linear in its presence, the lines are considerably steeper. This difference between the effects of the two inhibitors on the relationship between the solution rate of iron and pH may be associated with their preferential effects on different stages of the hydrogen-liberation process. This hypothesis was tested by a method based on the existence of a definite connection between  $\gamma$  and the nature of the slow stage in hydrogen liberation [4]. If the slow stage is recombination, then

$$\gamma_{II} = \frac{b_{II}}{b_a + b_c} \quad (2)$$

and if it is discharge, then

$$\gamma_I = \frac{b_0}{b_a + b_c} \quad (3)$$

where  $b_0 = 2.3 \frac{RT}{F}$ ,  $b_a$  is the slope of the E-log i curve for the anodic dissolution of iron, and  $b_c$  is the slope of the E-log i curve for the cathodic liberation of hydrogen.

The polarization curves needed for determination of  $\gamma_I$  and  $\gamma_{II}$  by Equations (2) and (3) were determined in 1 N HCl both in presence and in absence of additives (Fig. 2).• The experimental ( $\gamma_{exp}$ ) and calculated values of  $\gamma$  are given in the table.

Experimental and Calculated Values of  $\gamma$

Medium	$b_a$	$b_c$	$\gamma_{exp}$	$\gamma_I$	Deviation (%)	$\gamma_{II}$	Deviation (%)
Hydrochloric acid without additives	0.058	0.120	0.31	0.34	9	0.67	111
Hydrochloric acid + 0.1 g of anthranilic acid per liter	0.052	0.120	0.34	0.35	3	0.70	106
Hydrochloric acid + 1 g of tetrabutylammonium sulfate per liter	0.052	0.137	0.80	0.92	60	0.72	10

It is seen that the experimental value of  $\gamma$  for hydrochloric acid is in agreement with  $\gamma_I$ . In presence of anthranilic acid, the slope of the experimental log i-pH lot is equal to  $\gamma_I$  and differs greatly from  $\gamma_{II}$ . On addition of tetrabutylammonium sulfate the value of  $\gamma_{exp}$  is very close to  $\gamma_{II}$  and is several times as great as  $\gamma_I$ .

It follows that anthranilic acid has no significant influence on the kinetics of hydrogen evolution, and the determining stage, as for solutions without additives, is recombination of hydrogen atoms ( $\gamma_{exp} \approx \gamma_I$ ). On the other hand, addition of tetrabutylammonium sulfate changes sharply the kinetics of hydrogen evolution, with delayed discharge instead of delayed recombination.

This conclusion is consistent with the electrical properties of the additives used. Anthranilic acid, which is present in the solutions in question almost entirely in the form of undissociated molecules, may influence hydrogen evolution mainly by changes in the heats of adsorption of hydrogen atoms, and in the conditions for their interaction. Any direct influence on discharge (increase of the thickness of the double layer, creation of an electrical barrier by dipole orientation) should be slight, and should be observed only at high degrees of surface cover. In the same conditions, tetrabutylammonium sulfate is dissociated almost completely with formation of surface-active cations which are adsorbed on the iron-solution interface and create a positive field which retards hydrogen-ion discharge. As a result, the rate of discharge may become lower than the rate of recombination, as the influence of the field created by the cations on the latter is incomparably less.

Results obtained by other workers also indicate that the nature of the slow stage of hydrogen liberation may be changed by the action of cationic inhibitors. For example, Iofa and Liakhovetskaia [6] found that, in

• The polarization curves used for determination of  $b_a$  and  $b_c$  were determined for hydrochloric acid solution of one concentration only, as influence of solution composition on the slope may be disregarded in the relatively narrow pH range studied. This is confirmed by data for nickel [5].

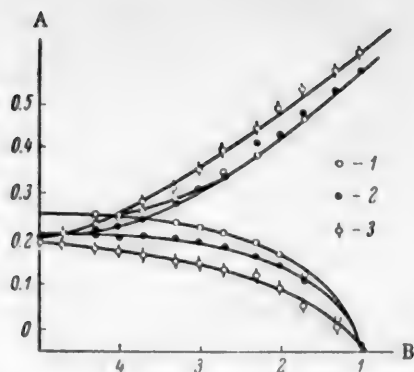


Fig. 2. Polarization curves for iron in 1 N hydrochloric acid solution. A) Potential  $E_{Fe}$  (v), B)  $\log i$ . 1) Without additives, 2) 0.1 g of anthranilic acid per liter, 3) 1.0 g of tetrabutylammonium sulfate per liter.

diffusion of hydrogen. If, as is assumed here, hydrogen liberation in presence of tetrabutylammonium sulfate proceeds by a delayed discharge mechanism, then access of atomic hydrogen from the polarization side should not affect the potential which becomes established at the iron surface in contact with a solution containing tetrabutylammonium sulfate; this was found to be the case by Bagotskaia and Frumkin. Since in pure acid the kinetics of hydrogen evolution is determined by recombination of hydrogen atoms, the equilibrium potential on the diffusion side must depend on the amount of atomic hydrogen entering from the polarization side of the membrane; this was found to be the case of Fischer and Heiling.

Tetrabutylammonium sulfate is not the only inhibitor capable of changing the nature of the delayed stage of hydrogen evolution. It is reported [9] that many nitrogenous organic inhibitors, which give rise to surface-active cations in acid media, retard the dissolution of iron without increasing its hydrogen saturation. Conversely, anionic inhibitors such as thiourea increase the hydrogen content of iron. It follows that in pickling processes, when hydrogen absorption by steel must be prevented, suitable additives are substances which behave like surface-active cations.

The fact that the nature of hydrogen overvoltage on iron can be changed indicates that the difference between the rate constants of hydrogen-ion recombination and of hydronium-ion discharge is not large. This, together with the fact that the equilibrium potential of iron in corrosion conditions is close to its zero point [10], is the probable cause of the fact that very many substances, differing in structure and charge, are inhibitors of the acid corrosion of iron.

#### SUMMARY

1. The nature of the relationship between hydrochloric acid concentration and the corrosion rate of iron is not changed by the addition of anthranilic acid. The slopes of the  $\log$  corrosion rate-pH plots indicate that in both cases recombination of hydrogen atoms is the slow stage in hydrogen evolution.

2. The slope of the  $\log$  corrosion rate-pH plots changes on addition of tetrabutylammonium sulfate, and its magnitude indicates that discharge of hydronium ions is the slow stage in hydrogen evolution in this case. Thus, tetrabutylammonium sulfate, and probably other cationic inhibitors also, not only raise the hydrogen overvoltage but alter its nature.

3. Changes of the nature of the slow stage in cathodic evolution of hydrogen on addition of cationic inhibitors should influence the amount of hydrogen absorbed by the iron; this is of practical significance in relation to choice of the pickling inhibitors.

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•Transliteration of Russian - Publisher's note.



## REACTIONS OF DIALKYLSILANE DIOLS WITH DIISOCYANATES

M. F. Shostakovskii, V. N. Kotrelev, D. A. Kochkin, S. P. Kalinina,  
and V. V. Borisenko

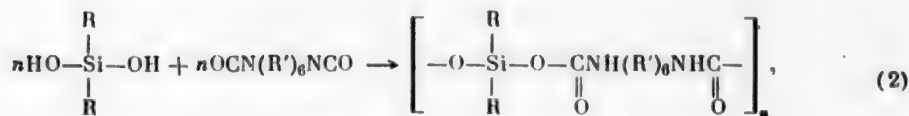
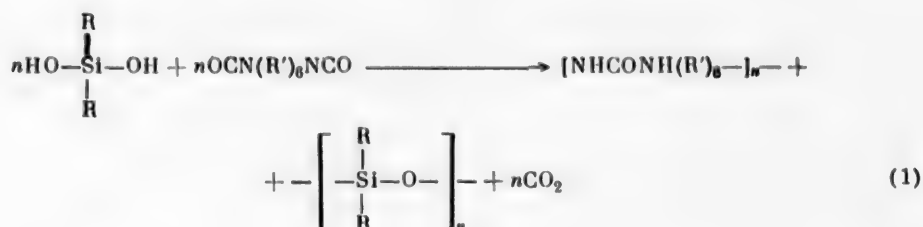
It is known that hexamethylene diisocyanate is used extensively in the production of polyurethanes, which have useful dielectric and physicomechanical properties. However, the heat resistance of polyurethanes is inadequate. It was therefore of interest to study the interaction of hexamethylene diisocyanate with organosilicon diols, in order to obtain organosilicon polyurethanes. Reactions of dialkylsilane diols with diisocyanates are not described in the literature.

The purpose of our investigation was a study of the reactions of dialkylsilane diols with diisocyanates, the examples chosen being diethylsilanediol or polyethylsiloxane diols and hexamethylene diisocyanate.

It was found that organosilicon polyurethanes are not formed as the principal reaction products.

The reactions of hexamethylene diisocyanate with diethylsilanediol or polyethylsiloxane diols lead mainly to the formation of polyureas and polysiloxanes (see Equation (1)). However, the formation of small amounts of organosilicon polyurethanes as by-products (see Equation (2)) is not precluded.

The reactions of dialkylsilane diols and polyalkylsiloxane diols with diisocyanates may be represented as follows:



where R = allyl or alkyl, and R' = -CH<sub>2</sub>-, -C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)-.

It is possible that the polysiloxanes, which are the main reaction products (Equation (1)) have a plasticizing effect on the polythiureas formed.

The reaction products are white powders, which may be molded into articles with electrical-insulation properties and of adequate mechanical strength.

Some physicochemical properties of the resins are given below.

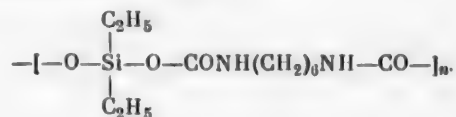
TABLE 1

Reactions of Hexamethylene Diisocyanate with Diethylsilanediol and Polyethylsiloxane-  
diol

Expt. No.	Components	Am'ts taken (g)	Temperature (°C)	Reaction time	Yield of reaction products	Elementary analysis (%)				
						C		H		Si
						found	calc.	found	calc.	found
7 u	Hexamethylene diisocyanate	14.9	130	6 hr	9 {	58.34	59.10*	9.79	9.85	—
	Water	8.0				58.47		9.76		
1 u	Hexamethylene diisocyanate	10.4	120—130	15 min	13.1	55.16	—	9.28	—	8.21
	Diethylsilanediol	7.4						9.21		8.44
	Aluminum chloride	0.18						—		—
Ditto	After extraction with alcohol and ether	Ditto	Ditto	Ditto	Ditto	56.21 56.39	55.3**	9.18 9.18	9.20**	0.60 0.85
Ditto	After extraction with ether	*	*	"	"	58.72 58.62	59.10*	9.53 9.63	9.85*	Traces
3 u	Hexamethylene diisocyanate	9.5	130	4 hr 30 min	9.6	56.88 57.09	—	9.20	—	Traces
	Diethylsilanediol	6.8						9.23		
	Chlorobenzene***	80.0						—		
6 u	Hexamethylene diisocyanate	17.0	130	6 hr	13.0	57.73 57.74	59.10*	9.37	9.85*	Traces
	Diethylsilanediol	12.1						9.14		
	Chlorobenzene****	135.0						—		
Ditto	After extraction with alcohol and ether	Ditto	Ditto	Ditto	Ditto	57.77 57.69	—	9.11 9.21	—	Nil
491	Hexamethylene diisocyanate	84.0	130	6 hr	30.0	55.04	—	8.89	—	15.29
	Polyethylsiloxanediol	200.0				54.88		9.11		15.71
Ditto	After extraction with ether	Ditto	Ditto	Ditto	Ditto	58.78 59.29	59.10*	9.35 9.54	9.85	Traces

\* Calculated for polyhexamethyleneurea of the composition  $-\text{[NHCONH(CH}_2\text{)}_6\text{]}_n-$ 

\*\* Calculated for the organosilicon urethane



\*\*\* Reaction products treated with alcohol and ether for purification.

\*\*\*\* Reaction products extracted with ethyl alcohol.

## EXPERIMENTAL

Starting materials. The following substances were used: 1) diethylsilanediol  $(C_2H_5)_2Si(OH)_2$ , white crystals, m.p. 94-96° [1]; 2) polyethylsiloxanediol  $HO-[Si(C_2H_5)_2O]_n-H$ , oily liquid, molecular weight 400-551,

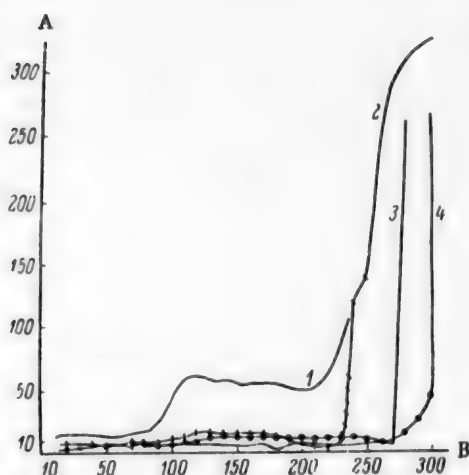
$n_D^{20}$  1.436-1.440; 3) hexamethylene diisocyanate  $OCN-(CH_2)_6-NCO$ ,  $n_D^{20} = 1.4538$ ,  $d_4^{20} = 1.069$ , b.p. 115° (5 mm).

**Experimental procedure.** A three-necked flask fitted with a mechanical stirrer and reflux condenser was charged with 10.4 g of hexamethylene diisocyanate, 7.4 g of diethylsilanediol, and 0.18 g of aluminum chloride as catalyst. The reaction mixture was heated to 120° for 15 minutes. When the reagents were mixed, the mixture became turbid and a gelatinous precipitate was formed. The precipitate was removed from the flask and treated with live steam to remove the unchanged components from the reaction products. The yield was 13.1 g

of a bulky solid which could be molded into various shapes. To determine the nature of the reaction between diethylsilanediol and hexamethylene diisocyanate, 2.3 g of the solid precipitate was extracted with ether and ethyl alcohol, or ether only, for 6-10 days. The reaction products were taken to constant weight both before and after the extraction, and analyzed for carbon, hydrogen, and silicon. Analyses showed that silicon was present in the reaction products before extraction. After the extraction silicon was not found. The composition of the precipitate after extraction with alcohol and ether (1.3 g) corresponded to polyurea, but the precipitate also contained a small amount of the reaction products of alcohol and hexamethylene diisocyanate (the analytical results are given in Table 1, Experiment 1 u).

The ether and alcohol extracts contained 0.6 g of liquid substance which, by analysis, corresponded to a polydiethylsiloxane resin of the composition  $-(C_2H_5)_2SiO)_n-$

Found %: C 46.66, 46.84; H 9.69, 9.57; Si 27.32, 27.40. Calculated %: C 47.05; H 9.80; Si 27.51.



Thermomechanical properties of the reaction products of hexamethylene diisocyanate and silane diols. A) Instrument scale readings, B) temperature (°). Experiment No. and molding pressure (°) respectively: 1) 3u and 220, 2) 3u and 300, 3) 7u, 4) 1u and 200.

TABLE 2

Certain Physicomechanical Properties of the Reaction Products of Hexamethylene Diisocyanate and Silane Diols

Expt. No.	Molding conditions		Characteristics of molded material						
	temp-erature (°C)	pressure (kg/cm <sup>2</sup> )	heat resistance, Vicat test (°C)	specific impact viscosity, Dienstat test (kg·cm/cm <sup>2</sup> )	Brinell hardness (kg/mm <sup>2</sup> )	surface resistivity (ohms)	volume resistivity (ohm·cm)	tan of dielectric loss angle at 10 <sup>6</sup> cycles/second	dielectric constant $\mu$
491	250	60	100	20-30	5.15	$1.1 \cdot 10^{14}$	$1.4 \cdot 10^{13}$	0.0064	3.4
					3.99	$1.1 \cdot 10^{14}$	$3.8 \cdot 10^{13}$	0.0060	3.1
					5.15	$1.1 \cdot 10^{14}$	$1.3 \cdot 10^{13}$	0.0062	3.5

The experimental results are summarized in Table 1.

Physicomechanical properties of the materials. The interaction products of diisocyanates with diethylsilanediol and polyethylsiloxanediol were molded under specific conditions (Table 2). The samples were molded into various shapes in presses with heated plates. Some physicomechanical properties of the molded material are given in Table 2. It is seen that the material has considerable mechanical strength and good insulating properties. The thermomechanical curves (see figure\*) show that the material undergoes irreversible deformation only when the temperature is raised to at least 250°; this shows that its heat stability is considerable.

#### SUMMARY

1. The reactions of alkylsilane diols with diisocyanates were studied, with diethylsilanediol, polyethylsiloxanediol, and hexamethylene diisocyanate as examples; the reaction products are white powders which may be molded into articles of good insulating and mechanical properties.

2. It was found that the principal reaction products are polyurea and polysiloxanes. However, the possibility of formation of small amounts of organosilicon polyurethanes as by-products is not precluded.

3. The reaction products of hexamethylene diisocyanate with silane diols or siloxane diols may be of practical interest.

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\*The thermomechanical properties were determined with the aid of Zhurkov's apparatus [2].

## PREPARATION OF 1,5-NAPHTHYLENEDIAMINE

S. S. Pen'kovskii and S. S. Kuznetsova

According to the literature, 1,5-naphthylenediamine may be prepared by three methods: reduction of 1,5-dinitronaphthalene [1-4], amination of 1,5-dihydroxynaphthalene by the action of heat and pressure on the latter in presence of ammonia and ammonium sulfite solution [5, 6], and amination of  $\alpha$ -naphthol [7] or  $\alpha$ -naphthylamine by decomposition of sodamide [8].

Of these methods for the preparation of 1,5-naphthylenediamine, the most convenient are by reduction of 1,5-dinitronaphthalene and by amination of 1,5-dihydroxynaphthalene. However, the former method involves separation of 1,5-dinitronaphthalene from 1,8-dinitronaphthalene, as it is not possible to obtain 1,5-dinitronaphthalene free from the 1,8 isomer by nitration of naphthalene. According to our results, the yield of 1,5-naphthylenediamine in this method does not exceed 11% of the calculated yield on the naphthalene taken.

The second method for the preparation of 1,5-naphthylenediamine, from 1,5-dihydroxynaphthalene, has not been studied sufficiently, and the possibilities of its industrial use are unknown.

According to different investigations, 1,5-dihydroxynaphthalene is prepared by alkaline fusion of 1-naphthol-5-sulfonic acid with caustic potash [9] or caustic soda [10], or by alkaline fusion of sodium naphthalene-1,5-disulfonate at 300-320° [11].

The present paper is the report of a study of the preparation of 1,5-naphthylenediamine from naphthalene-1,5-disulfonic acid and its sodium salt, by way of 1,5-dihydroxynaphthalene.

### EXPERIMENTAL

Preparation of 1,5-dihydroxynaphthalene. The preparation of 1,5-dihydroxynaphthalene was effected by alkaline fusion of naphthalene-1,5-disulfonic acid and its sodium salt with caustic soda. The effects of the reaction conditions (temperature, amount of alkali) on the yields of the final product were studied. The experiments were performed as follows. Water, caustic soda, and sodium naphthalene-1,5-disulfonate or the 1,5-disulfonic acid were introduced consecutively into a steel vessel, 500 ml in capacity, equipped with an anchor-shaped stirrer and a gas heater. A small amount of heat was evolved. The mass was heated to a definite temperature, and held at that temperature for various times.

In Series I, the apparatus was heated by means of a gas burner, and stirring of the reaction mass was discontinued at 160-180°.

In Series II and III, the stirring was continued throughout the fusion. In these series of experiments an oil bath was used to heat the apparatus.

The initially-mobile mass gradually thickened, and then turned into a powder. After the fusion was completed the apparatus was cooled, and hot water was added to dissolve the reaction mass. The solution was heated to boiling, filtered to remove impurities, and the filter was washed with water. The solution of the sodium salt of 1,5-dihydroxynaphthalene was neutralized with 93% sulfuric acid to a weak acid reaction to Congo paper. The precipitated 1,5-dihydroxynaphthalene was filtered off, washed with cold water on the filter to a negative reaction for  $\text{SO}_4^{2-}$  ions, and dried at 60-70°.

The product was analyzed for its 1,5-dihydroxynaphthalene content by the coupling reaction with phenyldiazonium chloride.

TABLE 1

Results of Experiments on the Preparation of 1,5-Dihydroxynaphthalene

Series	Amount taken			Fusion temperature (°C)	Fusion time (hours)	Moles of 93% H <sub>2</sub> SO <sub>4</sub> added for separation	Yield of 1,5-dihydroxynaphthalene (% of theoretical)
	72% Na salt of 1,5-NDS (moles)	91.93% NaOH (moles)	water (ml)				
I	0.1084	0.460	10	246—252	6	0.313	37.93
	0.1034	0.517	10	255—260	6	0.261	53.52
	0.1084	0.575	10	253—260	6	0.400	57.01
	0.1034	0.632	10	254—258	6	0.522	62.30
	0.1084	0.690	10	254—253	6	0.826	81.30
	0.1034	0.690	20	260—265	6	0.733	82.83
	0.1034	0.920	20	257—265	6	0.783	70.55
	0.1034	1.150	20	257—263	6	0.783	68.25
II	0.1084	0.690	20	320	2.00	0.435	79.26
	0.1034	0.690	20	317	2.00	0.435	79.69
	0.5422	0.450	100	312	0.34	2.174	80.62
	0.5422	0.450	100	310	0.75	2.174	80.69
	0.1084	0.690	20	321	6.00	0.435	83.27
	0.1034	0.690	20	320	2.00	0.435	85.72
III	0.1084	0.690	20	317	2.00	0.435	86.11
	0.5425	4.826	100	317—323	3.00	2.175	81.72
	0.5425	4.826	100	317—321	2.00	2.175	82.97
	0.5425	4.826	100	315—316	3.00	2.175	85.27
	0.5425	4.826	100	314—317	3.00	2.175	85.73
	0.5425	4.826	100	310—315	2.50	2.175	88.36
	0.5425	4.826	100	307—310	2.50	2.175	92.24
	0.5425	4.826	100	310—330	3.00	2.175	93.36

It follows from the experimental results in Table 1 that the highest yield of 1,5-dihydroxynaphthalene is obtained with 6.36 moles of alkali per mole of sodium naphthalene-1,5-disulfonate (1,5-NDS), or with 8.9 moles of alkali per mole of naphthalene-1,5-disulfonic acid. If the temperature of the reaction mass is raised above 270° by means of a naked flame, the yield of 1,5-dihydroxynaphthalene decreases owing to lack of stirring, and charring of the reaction mass at the bottom of the apparatus.

TABLE 2

Results of Experiments on the Preparation of 1,5-Naphthylene-diamine

1,5-dihydroxynaphthalene (moles)	Amount taken		Heating time (hours)	Yield of 1,5-naphthylene-diamine (% of theoretical)
	ammonia (moles)	sodium sulfite (moles)		
0.01265	0.318	0.0029	4	60.90
0.01265	0.318	0.0029	4	63.80
0.01265	0.318	0.0029	4	60.01
0.01265	0.318	0.0029	6	66.80
0.01265	0.318	0.0029	6	75.46
0.01265	0.318	0.0029	6	76.69
0.01265	0.318	0.0029	6	67.01
0.01265	0.318	0.0029	8	82.74
0.01265	0.318	0.0029	8	87.80
0.01265	0.318	0.0029	8	85.78
0.01265	0.318	0.0029	8	81.21



With gentler heating (Series II) it is possible to raise the reaction temperature and to increase the yield and concentration of 1,5-dihydroxynaphthalene. The use of naphthalene-1,5-disulfonic acid instead of its sodium salt (Series III) does not lower the yield or quality of the 1,5-dihydroxynaphthalene.

Slight frothing was observed in all the alkaline fusions, and in some experiments there was charring of the lower layers of the reaction mass, with partial formation of naphthalene and hydrogen sulfide (detected by their odor as the result of side reactions [12].

The 1,5-dihydroxynaphthalene, of m.p. 250-256°, was used for preparation of 1,5-naphthylenediamine.

Preparation of 1,5-naphthylenediamine. This compound was prepared by amination of 1,5-dihydroxynaphthalene by ammonia in presence of ammonium sulfite. 2 g of pure 1,5-dihydroxynaphthalene, 25 ml of 21.6% ammonia solution, and 1.2 ml of 15% solution of SO<sub>2</sub> in ammonia were heated together in a sealed tube and held at 125° for a definite time. At the end of the required time the tubes were cooled and opened; the large yellow crystals of 1,5-naphthylenediamine were filtered off and dried at 50-70°. The 1,5-naphthylenediamine content of the product was determined by diazotization (Table 2).

The results show that the heating time has a considerable effect on the yield of 1,5-naphthylenediamine.

Experiments on the amination of 1,5-dihydroxynaphthalene are now being performed in a steel autoclave, in order to prepare 1,5-naphthylenediamine in conditions similar to those used industrially.

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## INTERNATIONAL CONGRESS OF INDUSTRIAL CHEMISTRY IN ATHENS

The 30th International Congress of Industrial Chemistry was held in Greece,  
September 17-25, 1957

In all our minds, Greece is one of the sources of human culture. From our early days we become acquainted with her history, myths, and legends, with the memorials to her material culture - buildings, sculptures; we learn about her ancient philosophers and naturalists, poets and dramatists. European and Asian languages contain numerous Greek words. Every mathematician, physicist, chemist, and engineer uses Greek words and alphabet as scientific terms and symbols. In studying history and philosophy, every educated man becomes acquainted with the ideas of the Greek thinkers Democritus, Socrates, Plato, Aristotle, Heraclitus, and Epicurus.

The bonds which exist between Greece and Russia originated many centuries ago. They were greatly strengthened after the second half of the 18th century.

The mutual sympathies of the Greek and Russian peoples have been manifested at many stages of history.

The Soviet delegation went to the Congress in Athens, not only with the intention of becoming acquainted with the achievements of foreign chemical science and technology, but also with a feeling of deep interest in the history and culture of Greece, with feelings of sympathy for her people.

In addition to presentation of new research in the fields of chemistry and chemical technology, the Congress organizers aimed to strengthen personal contacts between scientists and technologists from different countries; this was effected by lobby discussions, and meetings at receptions and excursions.

About 1100 delegates from 31 countries attended the Congress. The greatest number came from France, whose chemists were the original conveners of the international congresses of industrial chemistry. Considerable numbers of delegates came from Yugoslavia, U.S.A., and the Federal German Republic.

Members of the Congress included many eminent scientists, including: from France, Prof. Bienaimé, Portevin, Aubry, Pelleron, Denivelle, Perrot, Lefevre, Moureau, Renault, Leveque, and others; from the U.S.A., Flett, Comings, Ames, and others; from Germany, Fischbeck, H. Franck (Democratic German Republic), Ehrmann, Simon (Democratic German Republic), Helferich, Barwasser, Gercke, and others; from Belgium, Van Rysselberge, Lefevre, Frenay, Meurice, Verhaiden, Leclerc; from Greece, Delyannis, Koujoumdjellis, Askitopoulos, Sakelaro, Karathanassis, and others; from Denmark, Soltoft; from Sweden, Lepsius and others. Among chemists from the People's Democracies, the following attended the Congress: Deputy Minister of Heavy Industry of Hungary, D. Szeker, and Prof. Koranyi (Hungary); Prof. Matiu and Gabriel (Rumania); Prof. Kucharski (Poland); Prof. M. Karschulin and Prof. D. Delic (Yugoslavia); Prof. D. Ivanov (Bulgaria), etc.

The Soviet delegation consisted of 9 persons: Academicians N. N. Semenov (Head of the Delegation) and S. I. Vol'fkovich, Corresponding Member AN SSSR N. M. Zhavoronkov, Prof. A. G. Kasatkin, Deputy Scientific Director of the State Institute of Applied Chemistry S. F. Bulushev, Head of the Laboratory of the Scientific Research Institute of Intermediates and Dyes, I. V. Aleksandrov, Senior Engineer of the Technical Administration of the Ministry of the Chemical Industry, D. L. Margolin, and Senior Scientist of the Karpov Physicochemical Institute, M. N. Shteding.

Apart from the plenary sessions, the work of the Congress was divided into 15 sections, classified as follows by the Organizing Committee: 1) analytical chemistry, microanalysis, laboratory equipment and apparatus; 2) processes and apparatus, plant equipment, heating, lubricants, production and application of cold; 3)

potable and industrial waters, waste-water purification; 4) solid, liquid, and gaseous fuels; 5) atomic energy in chemical industry; 6) ferrous and nonferrous metallurgy, precious metals, electrometallurgy; 7) inorganic chemical industry, electrochemistry, artificial fertilizers, silica gel, active carbons, catalysts; 8) constructional materials, cements, lime, road materials, glass, ceramics, enamels, brick and tile manufacture, refractories; 9) organic chemical industry, dyes, pharmaceuticals, photographic materials, explosives; 10) fats, soaps, detergents, waxes, essential oils, perfumery and cosmetics; 11) natural and synthetic resins, plastics, rubber and synthetic elastomers, varnishes, and pigments; 12) sugar production, the starch industry, enzymes, beer, and nonalcoholic drinks, wine making; 13) food products, baking, the dairy industry, the canning industry, fruit juices; 14) chemistry in agriculture, increase of soil fertility, insecticides, fungicides, herbicides, chemistry in animal husbandry; 15) organization of chemical education and scientific research, organization of production and sales; sources of raw materials, and markets.

The first plenary session was held in the ancient theater of Herodotus on the slopes of the Acropolis. The Congress was opened by introductory addresses by the President of the Society of Industrial Chemistry, F. Boudart, the President of the Permanent Committee for Congress Organization, R. Bienaime, and the President of the Organizing Committee of the 30th Congress, Professor of the Technical University of Athens, A. Delyannis. At the first session, the French delegate General P. J. Bergeron presented, on behalf of himself and of J. Yellot (U.S.A.), a paper of "The chemical aspects of the utilization of solar energy," comprising a review and general analysis of existing methods for the production of heat and cold from solar energy. Advances in solar-energy technology, including the application of photochemical processes and new synthetic materials for the absorption of solar radiation, were described in the paper. The construction of a special high-temperature furnace, operated with the use of parabolic mirrors, was reported. The author considers that in the near future, owing to the use of new synthetic materials, space heating will be effected more cheaply by solar energy than by other means. Solar energy could be rationally utilized for the production of low temperatures (down to  $-70^{\circ}$ ) by means of absorption refrigerators. The speaker noted the contribution of Soviet scientists to the development of solar-energy technology. The paper was presented from the "Association for Applied Solar Energy."

At another plenary session, the Technical Director of Elektrokemisk A/S (Oslo, Norway) M. Sem presented, on behalf of K. Sandvold and others, a paper entitled "Electric smelting of iron ores," which dealt with the development of electric furnaces and achievements in their design. He drew attention to the great importance of careful preparation of the furnace charge, and discussed the prospects for further improvements and cost reduction in the electric smelting of iron ores.

Professor of Liege University, E. Frenay, read a paper on "Classic and Floccular flotation," in which he considered the role of a number of flotation agents on the surface properties of various minerals. He presented his physicochemical concepts of floccular flotation with the use of air for separation of solid particles from pulps or colloidal systems, and suggested that further progress of the flotation method depends primarily on advances in delicate physicochemical methods for studying processes taking place between individual phases.

The Head of the Section for the Application of Radioelements at Saclay (France), P. Leveque, presented a paper on "Recent applications of radioelements and radiation," in which he reviewed the method and apparatus used for measurement of the thickness of extremely thin and thicker plates (up to 1 mm), gas velocities in pipes, displacements of sand and other soil strata, determination of soil humidity, etc.

A review paper on "Chemical products from petroleum" was given by G. Visser, Technical Director of S. A. Shell, Saint-Gobain, France. He discussed the synthesis of various products from methane, ethane, propane, and other materials. He stressed the great importance of the production of a number of important polymeric compounds such as polyethylene, polypropylene, polystyrene and others, from petroleum, and referred to the rapid development of petrochemical research in Europe.

At the last plenary session, Professor of Heidelberg University K. Fischbeck gave a paper on "Desalting of sea water." Serious attention has been paid to this question in recent years, in relation to the reclamation of new land for agricultural use in connection with the provision of fresh water for industrial undertakings, transport, habitations, and farms. The problem is also important for the utilization of lake and salt subterranean waters. The salt can also be utilized. The salt concentration in sea water can be lowered from 3.5% to 0.035% for the principal consumers. The speaker reviewed the desalting methods developed during the past decade in various countries, and presented a comparative economic evaluation of them. Of the 32 known methods, he

selected 9, of which he regards the following as the most promising: evaporation and distillation, the use of electrical ion-exchange diaphragm processes, and electrolysis. The thermocompressor method can be used to desalt sea water fairly cheaply. The use of solar energy for distillation and salt crystallization is in the pilot stage.

About 100 papers were read at the meetings of the sections; these included three papers by Soviet delegates: by N. N. Semenov on "Reactions of hydrocarbon oxidation," by S. I. Vol'fkovich on "The hydrothermal process of phosphate conversion," and by N. M. Zhavoronkov on "The organization of higher education in the USSR."

The Soviet delegates could not attend all the meetings of the sections, as these were too numerous; this brief review deals with only a few of the papers presented.

In the section on "Potable and industrial waters" papers were given by Prof. J. Kucharski (Warsaw) on "Neutralization of acid waste waters by means of limestone and dolomite filters," and by Prof. E. Leclerc and F. Edeline on "Flocculation of water contaminated by carbon residues."

In the section on "Atomic energy and chemical industry" a paper was given by L. Laurent (Center of Nuclear Studies, Saclay), entitled "Experimental techniques in the production of radioelements," in which he described the main methods for protection of workers against radiation; removal of liquid and solid radioactive materials from the reaction zone; and packaging of certain radioactive substances. This section also included a paper by P. Vertes (Director of Production Administration, the Atomic Energy Commissariat, Saclay) on "Choice of processes for the industrial production of uranium metal". He referred to the numerous methods for the production of uranium, some of which were described at the 1955 Geneva Conference and other scientific conferences, and drew attention to the insufficient exchange of experience and cooperation between the specialists of different countries in this field, which makes the selection of the best process for the production of metallic uranium difficult. He indicated the principal technical and economic requirements with regard to metallic uranium, and concluded that it is possible to carry out a comparative analysis of the different methods in order to select the most rational and promising.

The Czechoslovak delegates B. Chodura, H. Landspersky, V. Machacek, and J. Maly (Institute of Nuclear Physics, Academy of Sciences, Prague) gave a paper on "The preparation of uranium oxide crystals and study of their structure," in which they described the physicochemical conditions for the production of crystals up to 100  $\mu$  in size. Z. Dlouhy, J. Kutzendoreer, and J. Maly of the same institute presented a paper on "Kinetic studies of the adsorption and desorption of radioelements on surfaces."

In the section on inorganic chemical technology, presided over by P. Soltoft (Professor of Copenhagen University), the following papers were given at the first meeting: by J. M. Nicoletis (French Society for the Production of Sulfuric Acid by the Kashkarov Process), who discussed advances in the technology, equipment, and materials of sulfuric acid production; by Prof. S. Aries and P. Sachs (Aries Laboratories, U.S.A.) on "Production and uses of ultra-pure silicon," and the above-mentioned paper by S. I. Vol'fkovich.

The second meeting of the section included a paper by Dr. J. Barwasser (Director of Lurgi Ges. fur Chemie and Huttenwesen) on "Modern methods of pyrite roasting and sulfuric acid production." The speaker presented a detailed review of modern equipment and advances in sulfuric acid technology, and demonstrated numerous graphs and photographs. Prof. A. Simon (Technical High School, Dresden) spoke on "Desulfurization catalysts for illuminating and industrial gases, based on nonmetallic contact materials from mixed crystals (Raney phase analogs)" in which he discussed the effects of catalyst structure and dispersity on activity; he noted the great importance of pH and moisture content, and indicated methods for activation of these catalysts. Prof. A. Delyannis and Mlle. E. Piperoglou (Technical University, Athens) presented a paper on "Separation of hydroxides in relation to pH." They determined the conditions in which separation of the hydroxides of 2 and 3 cations is possible, and the influence of sulfates on the separation. G. Koranyi, Director of the Hungarian Research Institute for the Heavy Chemical Industry in Veszprem, reported on the results of his investigations, performed jointly with B. Balla, on the conversion of apatite by means of nitric acid for fertilizer production. They investigated a process for the simultaneous production of ammonium nitrate and dicalcium phosphate, and are studying a process for the manufacture of a mixed fertilizer containing nitrogen and phosphorus (approximately 20% each of N and  $P_2O_5$ ). A color film illustrating their laboratory and pilot-plant experiments was shown after the paper.

In the section "Organic chemical industry," presided over by Dejan Delic, Professor of the University of Belgrade, 18 papers were presented. N. N. Semenov gave a paper on "The mechanism of hydrocarbon oxidation reactions," which aroused great interest and was subsequently noted by the Congress organizers as one of the most important papers, illustrating the great significance of theory in industrial practice. L. Deffet (Director of the Belgian Research Center for the Explosives Industry and of the Brussels Institute of High Pressures) gave a paper on "Retarded-action explosives," in which he described the conditions for their production and safe use in underground mining operations. C. A. Haley (England) presented an extensive review on "Petrochemicals in Europe." He noted that at the present time one third of all the organic chemicals produced in Europe is derived from oil; this fraction is continuously increasing. According to his data, the production of petrochemicals in Western Europe in 1959 will be 1,000,000 tons, or roughly double the 1956 figure. A considerable proportion of this output will be used for polymer production. Prof. R. Perrot and Mlle. Y. Bourgau (France) reported the results of a study of the action of sulfonyl chloride on secondary amines. The paper by J. Kraft, R. Thermet, and L. Parvi (France) dealt with the chlorination of hydrocarbons, and the paper by E. Elchardus and L. Foulletier (Lyon), with the physicochemical principles of the production and analysis of chlorofluoro hydrocarbons. Prof. S. Ciborowski (Institute of General Chemistry, Warsaw) gave an account of a process, which has been worked out and introduced into production, for hydrogenation of acetone to isopropyl alcohol; the process is carried out in the gas phase with a catalyst consisting of copper and the oxides of aluminum and zinc; a process for dehydrogenation of isopropyl alcohol to acetone was also discussed. Engineer J. Herzenberg and Dr. Chem. G. Boccato (Italy) described the results of a study of the reaction mechanism in the synthesis of pyridine and its derivatives by the Baeyer-Chichibabin reaction. This synthesis has recently become very important, especially in the production of pharmaceuticals and of intermediates for polymer manufacture. The authors were able to increase the reaction rates and yields. Engineer Jacovic (Yugoslavia) reported on his work on the purification and separation of organic halosilanes by means of phenol. F. Velasco, Director of the Spanish Biochemical Institute, reported on two years of experience of ketone production by liquid-phase dehydrogenation of secondary alcohols. This method was developed in France and was first used on the industrial scale in Spain.

In the section "Resins and plastics," under the chairmanship of Prof. A. Matiu (Rumania), 5 papers were given. P. Talet, Director of a Paris research laboratory, described some polymerization reactions initiated by radiations, and the formation of graft polymers. The paper by R. Lepsius (Member of the Swedish Academy of Technical Sciences) contained a classification of natural and synthetic resins, based not only on their chemical composition and physical properties, but also on the possibilities of their technological conversion. F. Schouteden (Belgium) showed that when hydroxylamine reacts with polyacrylonitrile in the form of a powder dispersed in water, some of the nitrile groups are converted into hydroxamic acid groups. Engineer Vassiliou (Greece) described the results of his experiments on the separation of binary mixtures by the removal of certain ions. The systems studied were picric acid-hydrochloric acid, and glycerol-sodium chloride. The paper by G. Diamantopoulos (Greece) dealt with cellulose phosphate esters as ion-exchangers.

The section "Organization of chemical education, scientific research, and production" contained the following papers: by N. M. Zhavoronkov on "Organization of higher chemical education in the USSR," by Engineer Nicoletis (France) on "The Engineering Council and the Chemical industry," and by H. Redwood (England) on "Commercial research in the chemical industry." This last paper was devoted to an account of the work of a special organization on problems relating to raw materials supplies, markets, production units, and potentialities of new undertakings; these problems are becoming more important in capitalist countries without state planning organizations.

At the final plenary session the work of the Congress was briefly reviewed and several chemists were awarded certificates of honor for their fruitful scientific and technical activities.

A reception for the delegates by the Mayor of Athens was held during the Congress. The members of the Congress greatly enjoyed a remarkable presentation of Sophocles's tragedy "Antigone" in the ancient open-air theater of Herodotus. They were able to become acquainted with the modern industry and ancient culture of Greece in the course of various excursions to chemical, metallurgical, and mining undertakings, and to archeological excavations, historic monuments, and museums. The Soviet delegates had numerous opportunities of convincing themselves of the warm and friendly feeling of the Greek people, and in particular of Greek chemists toward Soviet chemists, and to reciprocate these sentiments.



Chemical literature published in the U.S.A., England, France, the Federal German Democratic Republic, was exhibited and sold at the Congress.

At the concluding banquet (organized on the seashore), the Congress organizers noted the great importance of numerous meetings between chemists of different countries for the progress of science and technology, drew attention to the rapidly growing influence of chemistry on the well-being and health of mankind, and called for a further increase of exchange of experience and scientific contacts. Special mention was made of the presence of the Soviet chemists, headed by the Nobel Laureate Academician N. N. Semenov who was honored by being appointed the Chairman of one of the sections by the Organizing Committee.

At the concluding meeting of the Congress it was announced that the next (31st) International Congress of Industrial Chemistry will be held in September 1958 in Liege.

The Organizing Committee of the forthcoming congress expressed the wish that it should be attended by Soviet chemists.

S. I. Vol'fkovich.



IVth CONFERENCE ON THE CHEMISTRY AND TECHNOLOGY OF  
SILICATES OF THE HUNGARIAN ACADEMY OF SCIENCES  
AND THE SCIENTIFIC-TECHNICAL SOCIETY OF  
BUILDING MATERIALS

The IVth Conference on the Chemistry and Technology of Silicates was held December 1957 in Budapest, at the Hungarian Academy of Sciences. The Conference was attended by members of scientific research institutes, universities, and industrial undertakings in Hungary, and by silicate specialists from the People's Democracies: USSR, Poland, Czechoslovakia, Rumania, Eastern Germany, and other countries.

The Conference was opened by Academician A. Geleji. The plenary session contained papers by Academicians of the Hungarian Academy of Sciences, M. Korach and J. Egervary, on heat economy in tunnel kilns, and mathematical analysis of heat transfer in firing. F. Sasvari, a section head of the Central Institute of Building Materials, discussed the applications of natural science to industrial problems.

The conference consisted of 5 sections, where more than 30 papers were presented on cement chemistry and technology, concrete, building materials, ceramics and refractories, glass, and methods of investigation. Considerable attention was devoted to quick-hardening and new cements, increase of mill output, decrease of fuel consumption in burning, and increase of the service life of plant. A paper communicated by Yu. S. Lur'e (Leningrad) was read; this dealt with water cooling of the sintering zone in rotary cement kilns. N. Kursovskil reported on the influence of certain substances on clinker formation.

The paper by M. Matousek (Brno) on the activation of slags by wet grinding was of interest in relation to the utilization of boiler slags. Equally interesting papers were given by B. Beke on closed-cycle grinding of cement, and by E. Lazar on the methods developed by him for the crushing of materials.

The section on cements contained papers by E. Bereczky on the corrosion of concrete and the role of puzzolana additions, and by the USSR delegates, P. P. Budnikov (Moscow) on the role of calcium sulfate in the hardening of hydraulic cements, and N. V. Il'ina (Leningrad) on the corrosion of chrome-magnesite bricks in the sintering zone of rotary cement kilns. S. Solacolu (Budapest) devoted his paper to the structure and hydraulic activity of blast-furnace slags. The paper by J. Albert on perlite and perlite light concretes was of special interest. The utilization of the enormous deposits of perlite in the production of light concrete is of great industrial importance, not only for Hungary but also for the USSR. Crushed perlite (a volcanic glass containing 70-75%  $\text{SiO}_2$  and up to 5% water; grain size 0.15 to 2.5 mm) is heated in a rotary kiln to 1100-1250° for 5-25 seconds; it becomes pyroplastic and swells by the action of the water vapor liberated from the perlite. The bulk density of the expanded perlite is about 130 g/liter. Light concrete made from this material (cement 250 kg/m<sup>3</sup>, and expanded perlite 140 kg/m<sup>3</sup>) has a bulk density of 440 kg/m<sup>3</sup>, and 28-day compressive strength of 17 kg/cm<sup>2</sup>.

Another interesting investigation, also carried out in the Institute of Building Materials, is the production of expanded clay gravel with a cellular structure (known as "keramsit"), used in the manufacture of light concrete. When the appropriate temperature is reached, a liquid phase first appears in the fusible clay, and swelling (formation of a porous structure) follows as the result of the distributed pressure of the gaseous decomposition and dissociation products of the clay components, and as the result of interaction of these products. The presence of organic impurities in the clay is of great significance in keramsit production. The whole firing regime is equally important. The clay does not swell in presence of iron oxide alone, or of organic substances without iron oxide.

J. Naray-Szabo described an electrical method for determination of the water-cement ratio. Among the papers on constructional materials were those by A. Czer on special concrete, by J. Sokegjarto on the micro-structure of magnesite refractories, and by K. Fedelinski on the role of crushing and granulometry in the refractory industry. T. Haase (Freiburg) discussed new theories of clay plasticity. The paper by R. Dollendorfer on optical investigations of the structure of ceramic materials is significant in relation to various silicate products.

The paper by K. Kuhne, a People's Prize winner, Head of the Laboratory of the Jena Glass Works, attracted much attention. He presented a detailed analysis of the properties of glass in relation to its composition. The paper by L. Gyorgy on the use of  $\text{Co}^{60}$  in studies of the erosion of the refractory blocks in glass furnaces was followed by a lively discussion. The paper by G. Koranyi (Director of the Scientific Research Institute of Chemical Industry) on the strength of glass, by M. Hubscher on foam glass, and by Stelian Lunge on new properties of ceramics made by glass from crystallization (known as glass porcelain), were discussed with considerable interest. F. Tamas presented a communication on ceramic ferrites.

Special interest was aroused by the papers by St. Nadasan from Bucharest on the rolling method for the production of blocks from cement paste, and by D. Varga on the stabilization of clays for the production of unfired constructional materials. The speaker was aware of our published papers on this subject. Work on clay stabilization has been carried out in the Hungarian Institute of Building Materials, and has attained practical importance. H. Geisler reported on work on lime-silica bricks, and A. Czer, on Hungarian bentonites and their activation. Both these papers are of great practical value. G. Kunst presented an interesting paper on Hungarian bauxite as filler for heavy concrete used as a protection against radiation. M. Gregor described his extensive work on dusts in cement shaft kilns, and their utilization in agriculture.

The Budapest Conference was well organized, and conducted at a high scientific level; it showed that silicate science in Hungary, and other countries of the People's Democracies, has become very important in the development of their national economies.

P. P. Budnikov

## BOOK REVIEWS

**SILICATE TECHNOLOGY** (2nd Collection of Research Papers) edited by Prof. Rudolf Barta. Prague, 1955 (285 pages)

**TECHNOLOGIE SILIKATU** (Sborník výzkumných prací II). Usporadal prof. ing. dr. Rudolf Barta, Praha, 1955.

In addition to papers from the Chair of Silicate Technology of the Prague Institute of Chemical Technology, the collection contains articles by workers from other scientific centers of the Czechoslovak Republic: the Glass Research Institute in Gradec-Kralov, the Institute of Constructional Materials in Brno, the Institute of Electrical Ceramics in Gradec-Kralov, the Institute of Heavy Ceramics in Rakovník, and the Chair of Silicate Technology of the Slovak Technical High School in Bratislava.

Czechoslovakia is very rich in silicate raw materials, which are being studied in all aspects. Several papers in the collection deal with this question.

State Prize Winner A. Kochanovská (Institute of Technical Physics, the Czechoslovak Academy of Sciences) carried out a detailed x-ray study of halloysite clays (from Mihalovec) and their dehydration products.

The paper by V. Satava and J. Skrdlik is an account of thermographic and x-ray investigations of high-silica raw materials (certain clays and marls) in relation to the production of lightweight, porous silicate blocks, "silikork." These authors also studied the processes taking place in the hydrothermal treatment of mixtures of lime and silica materials (by the steaming of a mixture, containing 150% water on the dry material, at 8 atm) and determined the influence of different factors on the formation of porous blocks. The production of good "silikork" requires a  $\text{CaO} : \text{SiO}_2$  ratio of 1:2. Addition of 1-2% HCl has a favorable effect on the strength of "silikork" boards. The hydrothermal reaction can be retarded by additions of sugar or sugar-containing substances. Up to 1% of sugar increases the strength and the bulk density of the final product. It was found that the calcium hydrosilicate formed under these conditions is the mineral gyrolite,  $2\text{CaO} \cdot 3\text{SiO}_2 \cdot \text{H}_2\text{O}$ . This valuable Czechoslovak building material should be of interest to our industry.

Czechoslovak scientists are making great efforts to find local raw materials to replace imports, and to ensure complete utilization of industrial waste products.

The paper by the late O. Kallauner, Jr. deals with the possibilities for the utilization of blast-furnace slags, which are very abundant in Czechoslovakia, and of which only 14% is used in the production of cements. Work on the production of cast blocks from slags is being carried out in the Institute of Constructional Materials (Brno).

R. Barta and Sv. Procházka showed that the wastes from the beneficiation of kaolin can yield up to 80% of the kaolinite present in them by simple methods, which mainly involve the dispersion of large aggregates of the kaolinite crystals.

R. Batar, together with scientists of the Kovotechna works (I. Binka and A. Pospíšil), presented the results of the first part of an investigation devoted to the search for readily available materials with electrical insulating properties at high temperatures. They performed detailed study of leakage currents on plates made from magnesite, fireclay, talc, kaolin, and other materials, in relation to grain size, molding pressure, and other factors, and showed that suitable compositions of domestic materials may be found for the production of articles not inferior to corundum in electrical properties.

Vl. Siske (Chair of Silicate Technology, Slovak Technical High School) showed, in an article entitled "Possibilities of the production of magnesian cements from local raw materials," that if dolomite is burned

in such a way that only  $\text{MgCO}_3$  is decomposed while  $\text{CaCO}_3$  remains unchanged, the magnesium oxide so formed has increased activity. Cements of the xylolith type obtained from this material are of high quality, despite the lower magnesium oxide content than that of Sorel cement.

R. Barta and Spicak continued their investigations of Slovak quartzites, and developed formulations for the production of high-quality Dinas bricks (with additions of iron oxide or iron scale). In another paper, R. Barta and M. Bartuska present numerous microphotographs of raw materials used for Dinas production in various countries (Czechoslovakia, USSR, England, USA), and give a classification of these materials.

A second group of articles is concerned with the production and properties of certain crystalline silicate materials. A paper of great interest is that by Z. Krzenek (Institute of Heavy Ceramics in Rakovník), who obtained mullite crystals in very different forms, which depended on the ratio of  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$  in the melt, and on addition of various oxides. The elongated four-sided crystals with inner cavities filled with glass matrix, obtained by the author, are especially remarkable.

R. Barta and M. Bartuska carried out a microscopic study of cordierite ceramics, and determined the conditions for the production of a material of the desired microstructure. They note that a synthetic cordierite glass, which may become "a new and reliable technical material," can be made in the electric arc.

The same group of papers contains an article by H. Arend and B. Brezina entitled "Some comments on the synthesis of magnesium titanates." They refer to the difficulty of obtaining a ceramic monomineral material containing any single magnesium titanate.

Much space is devoted in the book to articles which describe the work of Czech scientists on glass systems.

Dr. J. Voldan (Glass Research Institute) carried out extensive researches into the electrolysis of a number of glasses and numerous specimens of fused rocks and basalts. Mixed conductivity was observed in glasses containing iron oxides, which are the cause of electronic conductivity.

A contribution of great scientific value is the article by J. Glavac, who studied the phase diagram of the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ , in a search for suitable compositions of alkali-free glasses. He established the existence of a quaternary eutectic (anorthite-wollastonite-diopside-tridynite) of the composition  $\text{SiO}_2$  59.5,  $\text{Al}_2\text{O}_3$  14.2,  $\text{MgO}$  2.5 and  $\text{CaO}$  23.8%, with m.p.  $1160^\circ$ . This eutectic formed the basis of glasses with a thermal expansion coefficient of  $47\text{--}57.10^{-7}$ , and deformation temperatures above  $800^\circ$ .

In another paper, the same author describes a high-temperature rotational viscosimeter ( $10^2\text{--}10^6$  poise range); its error limit is estimated at 13%.

Soviet glass technologists should be interested in the article by M. Cap, entitled "Influence of  $\text{Li}_2\text{O}$  on the properties of glasses in the system  $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ ." Cap started with a glass composition corresponding to  $1\text{Na}_2\text{O } 1\text{TiO}_2 \text{ } 1\text{SiO}_2$ , in which sodium oxide was replaced by  $\text{Li}_2\text{O}$ . Lithium oxide was found to have a strong influence on the viscosity, coefficient of expansion, and softening temperature. Lithium oxide has become more widely used in glass making in recent years, and it is very important to continue work on various compositions containing lithium, as this should yield glasses of unusual properties.

Vl. Vitasil carried out an extensive study of vitreous systems of interest for enamel production. He devised a simple and accurate method for determination of the softening temperature of glass, and convenient techniques for observations of the wetting of metal surfaces by silicate melts and determinations of the contact angle. Four papers by Vitasil contain detailed descriptions of his methods, and the results of studies of glassy compositions in the system  $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ . He has proposed a formulation which may serve as a basis for the production of single-coat enamels on metals. It contains (in %):  $\text{Na}_2\text{O}$  19.33,  $\text{K}_2\text{O}$  12.0,  $\text{Li}_2\text{O}$  2.0,  $\text{CaF}_2$  1.00,  $\text{Na}_3\text{VO}_4$  0.2492,  $\text{TiO}_2$  33.67 and  $\text{SiO}_2$  33.0. It is seen that no boric anhydride is used.

It is good to see that the amount of silicate research in Czechoslovakia has increased considerably. This is clearly shown by a comparison of the two collections published in that country. • In our opinion, the title of the second collection - "Silicate Technology" - does not describe its contents quite accurately. It contains a considerable number of theoretical papers.

• See the review of the 1st collection in the journal *Glass and Ceramics*, 10, 12 (1955).

It should be noted that Czechoslovak scientists often work along independent lines and devise original techniques which yield accurate results with the use of simple methods. The scope of their work is also expanding continuously. In addition to research on glassy systems, where Czech scientists have made such important contributions, work is in progress on crystalline silicates.

Soviet workers on silicates must take note of the most important work published by the Institute of Czechoslovakia.

N. A. Toropov and V. P. Barzakovskii

Marschal Sittig, Sodium, its Manufacture, Properties and Uses. American Chemical Society Monograph. New York, Reinhold Publishing Corp., 1956, (529 pages).

Sodium has become an important chemical product. The present annual world production of this metal is about 136,000 tons. During the past 60 years the sodium industry has developed extensively, production methods have been greatly improved, the physical and chemical properties of sodium have been thoroughly studied, and the fields of application have been much extended. The invention of the Castner cell (1890) for the production of sodium by electrolysis of fused caustic soda, the Castner process for sodium cyanide, discovery of the cyanide process of gold extraction, and development of a process for the production of sodium peroxide by the oxidation of metallic sodium, all mark individual stages in the continuous growth of the sodium industry in Europe and America.

In the middle of the 1920's, the Downs cell for the production of sodium by electrolysis of fused common salt was developed. Shortly after this tetraethyllead was introduced in the USA as an antiknock additive to gasoline, and 60% of the sodium production of that country is now used in the manufacture of this additive. The power and performance of aircraft and automobile engines have been raised by the use of tetraethyllead as an additive.

The sodium industry has made particularly notable advances in the USA, where three leading chemical firms produce 120,000 tons of sodium annually.

M. Sittig, known for a number of his papers on the alkali metals, has written a book on the manufacture and use of sodium, which will be accepted with great interest by chemists working in this field.

The monograph "Sodium, its Manufacture, Properties, and Uses" is a serious work, and is the first book in the world's chemical literature to contain all the available data on the physical, chemical, and thermodynamic properties of sodium, manufacture and production techniques, storage and transport, uses and methods analysis, of interest to chemists and engineers. The literature data on the physical and thermodynamic properties are compiled fairly carefully, and are arranged in a form convenient for daily use. The text is clarified and augmented by 150 illustrations, including flow sheets, drawings, and photographs of equipment and operational techniques.

The periodical and patent literature of sodium is reviewed very thoroughly: the bibliography contains more than 2,000 references.

The book consists of nine chapters. Literature references are given at the end of each chapter.

The first, introductory chapter contains brief historical information on sodium, with some statistical data on the production of the metal in the USA and other countries.

The second chapter, "Manufacture of metallic sodium," deals with the thermochemical reduction process for the production of sodium, and its manufacture by electrolysis of fused caustic soda (the Castner process) and common salt (Downs process). A very brief review of different cells for the electrolytic production of sodium is given.

Only four pages are allotted to a description of the Downs cell, despite the fact that it occupies a leading and almost an exclusive position - 95% of the world production of sodium is made in Downs cells. A monograph on sodium should contain a full description of the Downs cell.

This chapter contains interesting literature data on the separation of sodium from its alloys.



The third chapter, "Solubility and alloy formation" deals with the solubility of sodium in liquid ammonia, in various organic solvents, in fused salts, and with the solubility of certain substances in sodium. The same chapter also contains data on the formation and properties of alloys of sodium and other metals, amalgams and their properties, the preparation and properties of lead-sodium alloys, potassium-sodium alloys, and certain other sodium alloys.

The fourth chapter, "Handling metallic sodium" deals with the storage, transport, and handling of metallic sodium. Chemical engineers will find much of value in this useful chapter. A brief account is given of pumps for liquid sodium. Safety rules for work with alkali metals are given in detail.

The uses of sodium are described in the fifth, sixth, and seventh chapters, comprising one third of the book. The author classifies the uses of sodium in two categories. One of these is based solely on the use of the unique physical properties of the metal, without chemical action. The other category comprises the uses of sodium based on its inorganic and organic chemical reaction.

Sodium is used on a large scale for the synthesis of tetraethyllead, and in the production of unique synthetic detergents, sodium peroxide, and cyanides.

During the second World War a new advanced method for de-scaling of metal surfaces by means of sodium hydride was developed in the USA, and adopted in the steel foundry industry. A method for the production of alcohols by the reduction of fatty acid esters with sodium was also developed in the USA. This provided new fields of application for sodium.

Much attention is being devoted at the present time to the use of sodium as a heat-transfer medium for nuclear units, including nuclear propulsion units for marine vessels.

The uses of sodium in metallurgy, including the production of titanium, are continuously extending. Reports have appeared in the American journals on the use of sodium for the production of zirconium, which is one of the most important materials for nuclear reactors. A plant for the manufacture of zirconium by sodium reduction commenced operation in the USA in 1957.

The eighth chapter, "Analytical chemistry of sodium," contains information on the analysis of sodium. This chapter consists of four sections: determination of sodium in solutions, determination of impurities in metallic sodium, and the use of sodium in analytical chemistry.

The ninth chapter, "Physical and thermodynamic properties of sodium," written by G. Thomson and E. Gareis, occupies a considerable part of the book (pp. 361-504) and contains useful information, but is in very small print and difficult to read.

On the whole, Sittig's monograph is a unique and valuable book on sodium, and it should be translated into Russian.

Received September 27, 1957.

I. Ia. Volkind

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•As in original - Publisher's note.

BRIEF HANDBOOK OF PHYSICOCHEMICAL DATA. Edited by K. P. Mischenko and A. A. Ravdel'. (Goskhimizdat, Leningrad, 1957). 2nd edition augmented.

The "Brief Handbook of Physicochemical Data" (2nd, augmented edition), compiled by N. M. Baron, E. I. Kviat, E. A. Podgornaia, and others was published in the second half of 1957.

The textbook is intended for the use of students in universities and technical colleges, postgraduate students, and teachers, and may be used in the teaching of physical chemistry.

In the new augmented edition, which comprises 112 pages (25 pages more than the 1st edition), the data are presented in the form of 78 numerical tables; 2 of these (37 and 72) are illustrated by appropriate diagrams. A list of literature references, more complete than in the first edition, is given at the end of the book. The book is completed by auxiliary tables of logarithms, necessary for physicochemical calculations, and a subject index, which is lacking in the first edition.

The 2nd edition has thus been augmented with new reference data.

The "Brief Handbook of Physicochemical Data" contains extensive factual data on various aspects of physical chemistry, noted in the review of the 1st edition,\* and there are some data from new sources.

The 2nd, augmented edition includes a number of new tables (2-11, 16, 62 and others). Moreover, some of the original tables have been supplemented with new numerical data.

All this gives a more complete and thorough appearance to the book.

There are several tables on radioactivity; this is a new section, not found in the first edition. Among these are tables entitled: "Radioactive Series," "Natural Radioactive Elements Outside the Principal Radioactive Families," "Some Nuclear Reactions," "Some Thermonuclear Reactions," etc. This information can be useful in studies of the most complex and topical problems of modern science.

Other information not found in the first edition includes data on the mean heat capacities of elements and compounds in the range 298-T° K, the saturated vapor pressure of mercury at various temperatures, hydrogen overvoltage, etc.

Attention must be drawn to certain defects and inaccuracies in the 2nd edition. On pages 9-12 element 86 should be given the more modern name of radon rather than radium emanation, especially as in the Mendeleev Table (pp. 4-5) and elsewhere (p. 87) the symbol of this element is given as Rn and not Em.

Some substances are classified sometimes as inorganic and sometimes as organic. Thus, in Table 14 CO, CO<sub>2</sub>, and CS<sub>2</sub> are included with inorganic compounds, and in Table 43, with organic.

Similar carelessness is found on p. 33, where typical halogen derivatives are included with oxygen compounds. In Table 49 it is not stated in what media the indicators give their colors (compare Table 33 of the 1st edition).

These contradictions and errors are confusing, and hinder proper use of the data.

On p. 27 the compilers use the obsolete terms "haloid-containing" and "haloid derivatives" (p. 36). They should be replaced by the more suitable and accurate term "halogen derivatives."

\*J. Phys. Chem. 30, 237 (1956).

Table 39 contains the following inconsistency: the viscosities of liquid benzene and glycerol are given for different temperatures, including 0°. In reality, both compounds are not liquids but solids at 0° (at 760 mm), and therefore their viscosity under these conditions has no physical meaning.

The chemical formulas of phosgene and hydrogen cyanide are incorrectly presented in Table 31.

The title of Table 23 should be changed, as its content has been greatly changed from the 1st edition. In the new edition, this table contains metals only (apart from boron), and not representatives of various classes of compounds, as in the first edition – salts (the chlorides of silver, sodium, and potassium), oxides (of aluminum, beryllium, calcium, and magnesium), and certain metals and nonmetals (sulfur, oxygen, and chlorine).

The densities of the alkali metals lighter than water have been unjustifiably rounded off in this table; this is particularly undesirable in the case of sodium (given as 1.0), especially as in this case it should float freely under water (having the same specific gravity). In reality, sodium floats on water, as it is lighter (sp. gr. of Na is 0.97).

We may conclude that the 2nd edition may be successfully used in studies of physical chemistry, in laboratories, and for practical physicochemical calculations (with due regard for all the errors).

I. G. Filatov.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY  
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.



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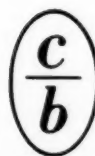
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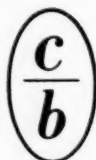
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